SYNTHESIS AND SPECTROSCOPIC STUDIES OF
SOMETI-ORGANOMETALLIC CARBONYL COMPLEGES

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Syntheses and Spectroscopic Studies of Some π-Organometallic Carbonyl Complexes

A Thesis

by

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Dedications

Mom, Dad

and

Yeok-Goh

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Abstract

The preparation and characterisation of a series of new π-$Mn(CO)_3$ and π-$Cr(CO)_3$ complexes are discussed. The benzoylcyclopentadienylmanganese tricarbonyl derivatives obtained are generally yellow in colour and melt at temperatures between 50° - 100°. The corresponding π-$Cr(CO)_3$ complexes are orange to red in colour and melt at higher temperatures. These complexes are stable in their solid state but decompose readily in solution.

The infrared spectra of these complexes have been studied both in CCl_4 and in Nujol mulls. A C_{3v} local symmetry is assumed for the $M(CO)_3$ moieties and the electronic effects of aromatic substituents on the ν(CO) vibrations are explained by the M.O. model. The electronic effects of the substituents on one ring are transmitted to the other via the ketonic carbonyl group as indicated by the corresponding shifts of the ketonic ν(CO) frequencies. The lower ν(CO) frequencies observed for the π-$Cr(CO)_3$ complexes are mainly due to the decrease of π-electron density on the benzene ring.

The electronic absorption bands of these complexes have been tentatively assigned on the basis of their shifts with substituent changes and by the comparison

of such bands with those of related complexes.

NMR spectral studies show that the π-character of the aromatic ring is not reduced by the electron-withdrawing effect of the $Cr(CO)_3$ group. It is suggested that the most stable configuration of the $Cr(CO)_3$ group is that in which the Cr atom is mainly bonded to the meta and substituent positions of the monosubstituted benzene ring.

The delocalisation of the unpaired spin in radical anions of these complexes is well illustrated by their ESR spectra. These spectra have been simulated and the spin densities calculated using McConnell's equation. Good agreement between experimental and theoretical spin densities has been obtained. Hyperfine splitting constants show that a substantial amount of the spin density is found on the manganese atom, and the para and ortho protons of the phenyl ring. No hyperfine lines have been observed for the meta or cyclopentadienyl protons.

The mass spectra of these complexes show a fragmentation pattern in which the CO molecules are lost first. The ability of the ionic structures to undergo intramolecular rearrangement process is facilitated by the active participation of the metallic orbitals with the π-orbitals of the ligand. The stability of the ions is dependent on the ring substituents. Where the substituent

is electron donating the ions are usually stabilised and vice versa. This is consistent with the view that the electron removed during ionisation belongs to a molecular orbital very largely associated with the metal atom.

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CHAPTER 1
GENERAL INTRODUCTION

GENERAL REMARKS

Organometallic π-complexes have been known since the discovery of Zeise's salt[1], $K(PtC_2H_4Cl_3)$ in 1827. However it was not until the early 1950's, following the accidental discovery of ferrocene[2,3], that remarkable progress in the field of organometallic chemistry was made. This outbreak of research activities is probably attributed to the intriguing nature of the metal-ligand bond and the potential of these complexes as synthetic intermediates and catalysts.

Many review articles on this field have since been published. These include a recent literature guide to organometallic chemistry, covering the years 1950-1970 inclusive, compiled by Bruce[4].

π-Cyclopentadienyl-Transition Metal Complexes.

Bis-π-cyclopentadienyl metal complexes.

Most transition metals have been shown to form bis-π-cyclopentadienyl metal compounds of the type $[(C_5H_5)_2M^n]X_{n-2}$ where n is the oxidation state of the metal M and X is a univalent anion. Neutral compounds $(C_5H_5)_2M$, however, are only important in metals of the first transition series. $(C_5H_5)_2Mn$ is found to be ionic[5].

The most convenient preparative route is by the

reaction of anhydrous metal chloride with a solution of sodium cyclopentadienide in tetrahydrofuran or a polyether[6].

$$FeCl_2 + 2C_5H_5Na \longrightarrow Fe(C_5H_5)_2 + 2NaCl.$$

This method can be used for preparing both transition and non-transition metal analogues. The Grignard type[7] reaction is also a useful method though the yields are often low and the products difficult to isolate. The reaction can be written in a general form,

$$2C_5H_5MgBr + MX_n \longrightarrow (C_5H_5)_2MX_{n-2} + 2MgBrX$$

where X is a halogen.

The aromaticity of the C_5H_5 rings in ferrocene has been demonstrated by the following observations[8],

a) the inability of ferrocene to react with maleic anhydrides

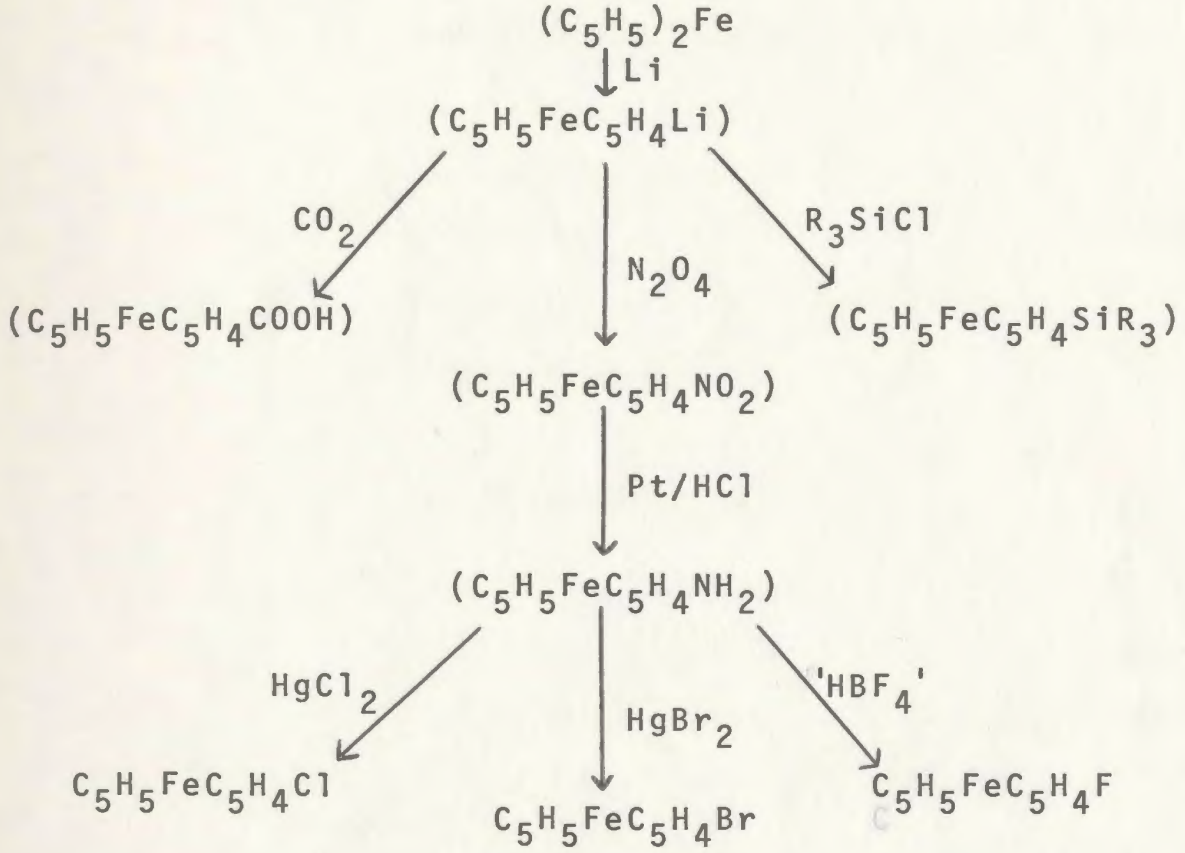
b) the inability of ferrocene to be hydrogenated in the presence of nickel catalyst

c) the readiness of ferrocene to undergo typical aromatic substitution reactions such as Friedel-Crafts acylation.

d) the ease of metallation by n-butyllithium

and e) a singlet is observed at 5.9 τ in the NMR spectrum of ferrocene[9].

The aromatic character of ferrocene enables a wide variety of derivatives[10] to be prepared, e.g.,



Recent solvolytic studies[11,12] of some metallocenylcarbinyl derivatives show that α-metallocenyl carbonium ions are unusually stable. Cais[13] successfully isolated stable salts of these ions, e.g. $(C_5H_5FeC_5H_4CHC_6H_5)^+BF_4^-$. The planar structure proposed by Richards and Hill[11] and Pettit et al.[14] has been rejected by Cais[13] and more recently by Gleiter and Seeger[15] and Watts et al.[16]. It has been suggested that the fulvene ligand is distorted from planarity.

Apart from the role of bonding and stabilising the ions, the iron atom may also participate directly in the substitution mechanism. It has been proposed[17] that in the electrophilic substitution reaction of ferrocene, the iron atom is first oxidised to form a ferrocenium cation intermediate. Several mechanisms have been proposed to explain these chemical reactions. Basically, it is believed that the π-electrons are more delocalised in the ionic intermediate than in the neutral compound.

π-Cyclopentadienyl metal Carbonyls.

Following the preparation of a large number of binuclear cyclopentadienyl carbonyl compounds of Mo and W[18], a large number of simple mononuclear species has been prepared, e.g. $C_5H_5V(CO)_4$, $C_5H_5Mn(CO)_3$ and $C_5H_5Co(CO)_2$. They are either prepared by direct carbonylation under pressure in an autoclave or by reacting the metal carbonyl derivative with alkali metal cyclopentadienide[21].

$$(C_5H_5)_2Mn \xrightarrow{CO} C_5H_5Mn(CO)_3$$

$$Mn(CO)_5Br + Na^+C_5H_5^- \xrightarrow{THF} C_5H_5Mn(CO)_3 + NaBr + 2CO\uparrow$$

Kozikowski et al.[22] found that $C_5H_5Mn(CO)_3$, like ferrocene, is very stable to air, iodine, hydrogen chloride and maleic anhydride. The infrared spectra of ferrocene

and $C_5H_5Mn(CO)_3$ are markedly similar in regions where the cyclopentadienyl ring absorbs. Furthermore, $C_5H_5Mn(CO)_3$ undergoes the same aromatic substitution reactions as ferrocene except perhaps a little less readily. The order of decreasing ease of reactivity in Friedel-Crafts acetylation is found to be,

$$C_6H_5OH > (C_5H_5)_2Fe > CH_3OC_6H_5 > CH_3C_5H_4Mn(CO)_3 > C_5H_5Mn(CO)_3 > C_6H_6.$$

Although the $Mn(CO)_3$ is essentially an electron--withdrawing group, the cyclopentadienyl ring is still capable of showing much aromatic character. Most of the derivatives of the type $X\text{-}C_5H_4Mn(CO)_3$ have been prepared by the methods previously discussed for ferrocene. Acetylcyclopentadienylmanganese tricarbonyl, for example, has been prepared by Friedel-Crafts reaction[22]. Reduction of this ketone using $LiAlH_4$ gives the corresponding secondary alcohol[23] which can be dehydrated to give an alkene derivative and an ether.

$$CH_3COC_5H_4Mn(CO)_3 \longrightarrow CH_3CH(OH)C_5H_4Mn(CO)_3 \longrightarrow$$

$$CH_2{=}CHC_5H_4Mn(CO)_3 + (CO)_3MnC_5H_4CH(CH_3)OCH(CH_3)C_5H_4Mn(CO)_3$$

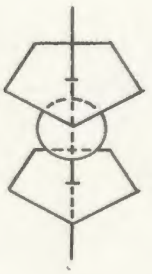
In the presence of ultraviolet light the CO molecules can be replaced by suitable ligands. For example, $C_5H_5Mn(CO)_2L$ where L = triphenylphosphine, pyridine and

tetrahydrofuran, have been obtained. McEwen et al.[24] proposed that the mechanism probably involves the formation of a sixteen-electron intermediate $C_5H_5Mn(CO)_2$ and that the reaction is of the S_N1 type. Displacement of two and three CO groups have also been achieved using PPh_3[25] and C_6H_6[26] respectively; the latter gives C_5H_5Mn-C_6H_6, a mixed sandwich complex.

Bonding and Structure.

X-ray diffraction studies[27,28] show that crystalline ferrocene has a staggered conformation whereas ruthenocene and osmocene are eclipsed.

Staggered



Eclipsed

In the vapour state, however, an eclipsed conformation is favoured by ferrocene[29].

The nature of the metal-ligand bond has been of considerable interest and critically discussed by Cotton and Wilkinson[30]. Dunitz and Orgel[31] were among the first to use an M.O. treatment to discuss the bonding of ferrocene.

They classified the ligand and metal orbitals according to their symmetries and then combined them correspondingly to form a set of molecular orbitals. The molecular orbitals of the two rings having molecular point group D_{5d} are A_{1g}, A_{2u}, E_{1g}, E_{1u}, E_{2g}, and E_{2u} which can combine with the $A_{1g}(4s, 3d_z2)$, $A_{2u}(4p_z)$, $E_{1g}(3d_{xz}, 3d_{yz})$, $E_{1u}(4p_x, 4p_y)$, and $E_{2g}(3d_{xy}, 3d_{x^2-y^2})$ orbitals of the metal. The molecular orbitals obtained by Dunitz and Orgel fail to account for the diamagnetism in ferrocene. Moffitt[32] remedied this discrepancy by allowing a certain amount of mixing of the $3d_z2$ and 4s metal orbitals. However, this treatment is too qualitative and was later modified by introducing some quantitative approximations to the energy levels[33]. More recently Schustorovich and Dyatkina[34] have carried out some elaborate calculations on ferrocene and they suggested that the M.O.s of E_{1g} and E_{1u} symmetries are all bonding and are responsible for the stability of ferrocenyl and half sandwich complexes. The E_{1g} bonding orbital transfers charges from the metal to the ring while the E_{1u} bonding orbital transfers charges from the ring back to the metal. This concept of metal-ligand bonding in ferrocene and $C_5H_5Mn(CO)_3$ is capable of explaining both the physical and chemical similarities of the two complexes.

$C_5H_5Mn(CO)_3$ has a much lower symmetry than ferrocene and the bonding can only be approximated by considering

the M.O.s of the molecule in parts. Bohn and Haaland[29] assumed the $Mn(C_5H_5)$ group to have C_{5v} symmetry and the $Mn(CO)_3$ group to have C_{3v} symmetry. Though these assumptions have been supported by crystallographic studies[35,36] of the molecule, it cannot be assumed that the degeneracies permitted in C_{5v} symmetry will not be perturbed by the presence of a C_{3v} symmetry in the other part of the molecule and vice versa.

π-Arene-Transition Metal Complexes.

Bis-π-arene metal complexes.

The first type of arenechromium complex was obtained by Hein[37] using a Grignard reaction. Zeiss, Tsutsui and Herwig[38,39] studied the mechanism of this reaction. They proposed that the intermediate formed is bis-π-benzene-chromium cation but they did not isolate it. It was Fischer and Hafner[40] who first reported the synthesis of this π-complex. The reaction involves reduction of a suitable metal salt with aluminium powder, followed by the addition of an arene ligand to the metal. This is catalysed by anhydrous $AlCl_3$.

$$3CrCl_3 + 2Al + AlCl_3 + 6C_6H_6 \longrightarrow 3[(C_6H_6)_2Cr]^+(AlCl_4)^-$$

The neutral bis-π-benzenechromium is then obtained by

reducing the cation with sodium dithionite or by a disproportionation process in aqueous alkaline solution.

$$[2(C_6H_6)_2Cr]^{+} \xrightarrow{H_2O} (C_6H_6)_2Cr + 2C_6H_6 + Cr^{2+}$$

The above preparative method has been used to prepare arene complexes of most d-block transition metals.

Generally, neutral bis-π-arene metal complexes are more reactive than the corresponding bis-π-cyclopentadienyl metal complexes. Attempts to acylate, metallate and nitrate often give decomposition products[41]. Whether the substitution products have actually been formed and decomposed under the reaction conditions or the reagents are unstable is difficult to predict. Due to the instability of these complexes, their chemistry has not been fully exploited.

π-Arene metal carbonyls.

Mononuclear arene carbonyls, in particular the tricarbonyls, are normally prepared by direct reaction of the metal carbonyl with the arene derivative at the reflux temperature of a co-ordinating solvent such as diglyme[42,43].

$$M(CO)_6 + C_6H_5X \longrightarrow (C_6H_5X)M(CO)_3 + 3CO\uparrow$$

where X is preferably a charge donating substituent and

M = Cr, Mo, W.

Strohmeier[44] found that the most suitable temperature for this type of reaction is just below the decomposition temperature of the complex. However, substituents like -COOH, -CN, or -CHO tend to promote total decomposition of the metal hexacarbonyl[42,45]. The (benzoic acid) chromium tricarbonyl, for example, cannot be prepared by this method.

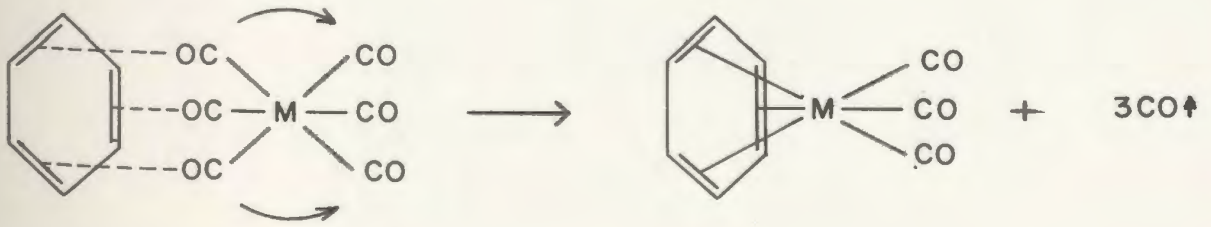
A mechanism for the formation of arene-metal tricarbonyl has been proposed by Fischer et al.[43] in which the equilibrium

$$M(CO)_6 + Ar \rightleftharpoons ArM(CO)_3 + 3CO\uparrow$$

is suggested and the equilibrium constant is given by

$$K = [M(CO)_6][Ar]/[ArM(CO)_3][CO]^3.$$

They proposed an S_N2 "Walden Inversion" type of mechanism in which the three CO molecules are expelled on the side of the metal opposite the approaching arene group, followed by the inversion of the remaining three CO molecules.



This mechanism has been supported by Brown et al.[46] who found that in the case where M = Mo, the reaction is rigorously first order in $Mo(CO)_6$.

The preparation of arenechromium tricarbonyl can also be carried out by the use of $L_3Cr(CO)_3$ instead of $Cr(CO)_6$ where L is generally a Lewis σ-base which can be replaced readily by the π-acid(arene). The addition of a Lewis σ-acid, BF_3, then removes the displaced σ-base from the equilibrium of the reaction. Öfele[47] used $(\gamma\text{-picoline})_3Cr(CO)_3$ to prepare mono-halobenzenechromium tricarbonyls, while Kaesz et al.[48] used $(NH_3)_3Cr(CO)_3$ to prepare cyclo-octatetraenechromium tricarbonyl. Both these methods have their own merits which vary from system to system. For example, Rausch et al.[49] found that whereas $Cr(CO)_6$ and $(\gamma\text{-picoline})_3Cr(CO)_3$ were unsuitable for preparing styrenechromium tricarbonyl, these reagents were generally more applicable for most other aromatic systems.

The chemical reactivity of the aromatic ring has been found to be greatly affected by complexation of the ring with a $Cr(CO)_3$ group. (Benzoic acid) chromium tricarbonyl, for example, is found to be a stronger acid than benzoic acid[45,50]; (aniline) chromium tricarbonyl is a weaker base than aniline[43] and chlorobenzenechromium tricarbonyl readily undergoes rapid nucleophilic substitution to yield (anisole) chromium tricarbonyl[45]. These

results tend to suggest that the $Cr(CO)_3$ group withdraws electrons from the aromatic ring. On the other hand, the rate of solvolysis of (benzylchloride) chromium tricarbonyl[51] and the rate of hydrolysis of (benzylalcohol) chromium tricarbonyl[52] have been shown to be about 10^5 times faster than the corresponding rates of the uncomplexed ligands. These increased rates may be due to the formation of very stable carbonium ion intermediates in which the central metal actively participates. Alternatively, they may be interpreted in terms of electron donation from the $Cr(CO)_3$ group into the π-orbitals of the aromatic ring.

Semiempirical M.O. calculations[53,54,55,56] have shown that there is in fact, a net withdrawal of π-electrons from the ring by the $Cr(CO)_3$ group and that a net positive charge is left on the σ-orbitals of the ring carbon atoms in the ground state. This has been supported by the observed direction of the metal-ring dipole moment in arenechromium tricarbonyl complexes[57,58].

Both the arene ring and the carbonyl groups in arenechromium tricarbonyl complexes can undergo displacement reactions. The arene ring in the complex exchanges readily with a labelled arene group under ultraviolet radiation[59].

$$ArM(CO)_3 + Ar^* \xrightarrow{uv} Ar^*M(CO)_3 + Ar$$

The rate expression derived by Strohmeier[60] is

$$K = k_1[ArM(CO)_3]^2 + k_2[ArM(CO)_3][Ar^*]$$

where $k_1 >> k_2$. It is assumed that each of the two rate determining steps involves the formation of transition intermediates. The carbonyl groups can be exchanged with other ligands such as ethylene, acetylene and pyridine[61], for example,

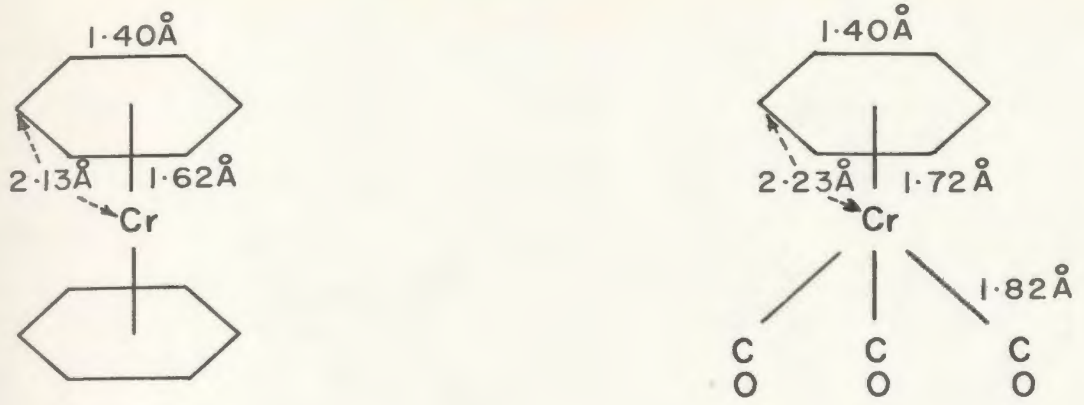
$$ArM(CO)_3 \xrightarrow[C_2H_4]{uv} ArM(CO)_2(C_2H_4)$$

Bonding and Structure.

Jellinek[62], using X-ray studies, found that the benzene rings in bis-π-benzenechromium show alternate C-C bond lengths. This led him to believe that the molecule has a three-fold and not a six-fold axis. Cotton et al.[63], however, carried out similar X-ray studies and concluded that there is only a slight difference in the C-C bond lengths which may be due to the presence of orientation disorder in the crystal. This is consistent with electron diffraction study results obtained by Haaland[64] who found that bis-π-benzenechromium in its vapour state shows equal C-C bond lengths.

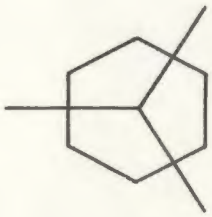
It is generally accepted that the molecule has D_{6h} symmetry[65] and the ordering of energy levels has been correspondingly approximated in a way similar to that made for ferrocene[66]. The main difference between the energy level diagrams of bis-π-benzenechromium and ferrocene is perhaps that the chromium atomic orbitals are of higher energies than those of iron. Furthermore, the M.O.s of the benzene ring are lower than those of the cyclopentadienyl ring. These differences suggest that the donor-acceptor interactions in bis-π-benzenechromium contribute less to the metal-ligand bonding than in ferrocene. This also explains the lack of basic properties of the former as compared to the latter[22].

The structure of benzenechromium tricarbonyl has been determined by X-ray studies[67]. It is shown that all the benzene carbon atoms are equally distant from the chromium atom and that the plane of the benzene ring is parallel to the plane of the three carbon atoms of the $Cr(CO)_3$ moiety. Similar conclusions have been obtained by Bailey and Dahl[68] who showed that the C-C bond lengths of benzene ring in benzenechromium tricarbonyl and bis--π-benzenechromium are equal within experimental error ($1.40 \pm 0.02\text{Å}$).



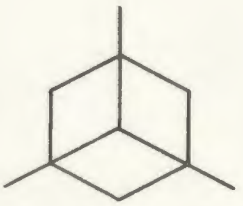
It can be seen from the diagram above that the arene-metal bond length in the former is greater than that in the latter. It is difficult to explain the equal C-C bond lengths in these two complexes since it has been shown that the $Cr(CO)_3$ group is a more effective electron withdrawing group than the C_6H_6Cr group[58,69]. The greater metal-ring distance observed in benzenechromium tricarbonyl is consistent with calculated metal-ring bond dissociation energies[70]. This may be due to a smaller contribution of the $Cr(CO)_3$ group to the metal-ring bond via back-donation than the C_6H_6Cr group.

If the central metal in benzenechromium tricarbonyl is assumed to have octahedral bonding, then two conformations are possible, viz



(a)

Staggered



(b)

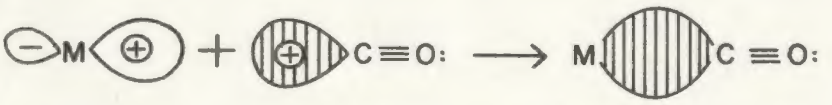
Eclipsed

Anisolechromium tricarbonyl and o-toluidinechromium tricarbonyl have been shown to have the eclipsed conformation[71,72] and it is suggested that electron donating substituents make it favourable for the electron-rich ortho and para positions of the monosubstituted benzene ring to be bonding centres of the metal. This electronic effect will be in competition with steric effect which tends to have a reverse effect[73,74], for example, benzenechromium tricarbonyl and hexamethylbenzenechromium tricarbonyl are found to have the staggered conformation and no indication of three-fold distortion of the aromatic ligand is observed[75]. However, these structural features have been deduced from X-ray studies where crystal forces have a significant effect on the results. As such it cannot be extrapolated to include solution state studies.

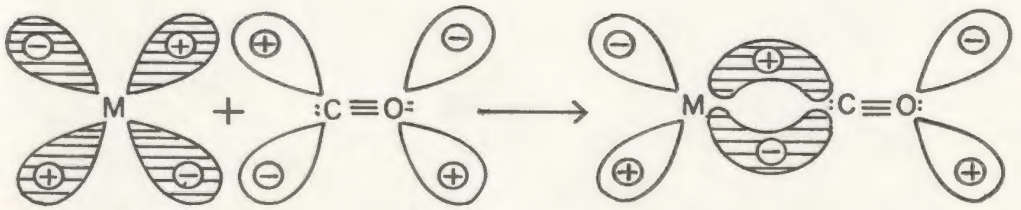
Bonding in Metal Carbonyls

The bonding between transition metals and carbon

monoxide is often exemplified by the discussion of octahedral metal carbonyls such as $Cr(CO)_6$[76]. In such cases, the bonding generally involves the σ-donation of lone pairs of electrons on the carbon atoms to the vacant metallic orbitals. This build-up of negative charges on the central metal is removed by 'back-donation' from the filled metallic d-orbitals to the low-lying vacant antibonding π-orbitals of the carbon monoxide. This may be pictorially represented as shown[77].



(a) OC ⟶ M σ-bond formation



(b) M ⟶ CO dπ-pπ* 'back-donation'

This σ-bonding and 'π-back-bonding' stabilises the bonding between weakly basic ligands and transition metals having filled d-orbitals. Such a mechanism is often known as a synergic effect.

The metal-carbonyl bonding in $M(CO)_3$ having C_{3v} symmetry is different from the $M(CO)_6$ molecule which

has O_h symmetry. Each of the three CO molecules has one σ- and two π-orbitals involved in the metal-ligand bonding. The three orbitals on each CO combine to give a set of M.O.s which can interact with the appropriate metal orbitals. Berndt and Marsh[78] found that the Mn-C≡O bond angles show systematic deviation from linearity and the same has been observed in Cr-C≡O by Bailey and Dahl[68].

	OC-M-CO	M-C≡O
$C_5H_5Mn(CO)_3$	91°, 91°, 94°	178°, 180°, 176°
$C_6H_6Cr(CO)_3$	89°, 89°, 86°	180°, 179°, 179°

Kettle[79] suggested that this bonding is a function of the difference in population of the two π* acceptor levels of the carbonyl groups.

CONCLUSION

The nature of the π-bond between the orbitals of transition metals and conjugated hydrocarbons, simple as it appears, is by no means well understood. In particular, the bonding between the $Cr(CO)_3$ moiety and the arene ring is often visualised as a withdrawal of π-electrons from the ring orbitals to the metal orbitals[80]. However, the transmission of π-substituent effects of the ring has not been observed to be significantly reduced on complexing

with $Cr(CO)_3$. Indeed more studies in this field need to be carried out and for this reason and others the present project has been undertaken.

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CHAPTER 2

SYNTHESIS

DISCUSSION

A series of new compounds of the type $XC_6H_4COC_5H_4Mn(CO)_3$ where X = H, CH_3, OCH_3, OH, Cl and F, were synthesised by Friedel-Crafts benzoylation of cyclopentadienylmanganese tricarbonyl.

The basic reaction steps are illustrated by the following equations.

$$Mn_2(CO)_{10} + Br_2 \xrightarrow[\text{room temp.}]{\text{THF}} 2Mn(CO)_5Br$$

$$Mn_2(CO)_{10} + Br_2 \xrightarrow[\text{reflux}]{\text{THF}} [Mn(CO)_4Br]_2 + 2CO\uparrow$$

$$Mn(CO)_5Br + Na^+C_5H_5^- \xrightarrow{\text{THF}} \pi\text{-}C_5H_5Mn(CO)_3 + NaBr + 2CO\uparrow$$

$$[Mn(CO)_4Br]_2 + Na^+C_5H_5^- \xrightarrow{\text{THF}} 2[\pi\text{-}C_5H_5Mn(CO)_3] + 2NaBr + 2CO\uparrow$$

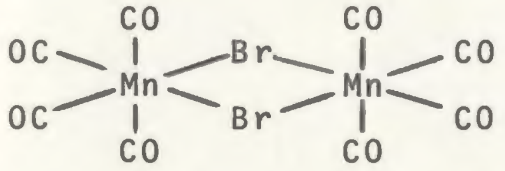
$$\pi\text{-}C_5H_5Mn(CO)_3 + XC_6H_4COCl \xrightarrow[CH_2Cl_2 \text{ or } CS_2]{AlCl_3} XC_6H_4COC_5H_4Mn(CO)_3$$

These complexes are relatively stable to air in the solid state but readily decompose in the liquid state or in solution.

In the bromination of di-manganese decacarbonyl , it is found that when the reaction mixture is allowed to react at room temperature, the product is $Mn(CO)_5Br$[1]. However, if the reaction is carried out at the reflux

temperature of THF, copper-coloured crystals are obtained in 80% yield. These crystals are highly insoluble and stable in air up to about 290°. The mass spectrum of this compound is consistent with the structure $[Mn(CO)_4Br]_2$ obtained by Abel and Wilkinson[2] in the thermal decomposition of $Mn(CO)_5Br$ in petroleum ether (100-120°), (40% yield).

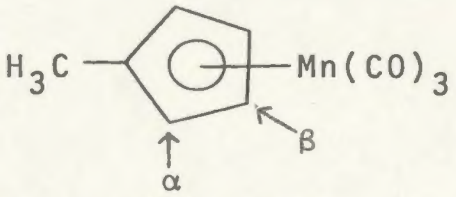
This dimer is found to be a better starting material than $Mn(CO)_5Br$ in the preparation of π-$C_5H_5Mn(CO)_3$. Perhaps the bridging structure of this molecule renders it more susceptible to attack[3].



The Friedel-Crafts benzoylation procedure has been described by Pleszke and Fischer[4]. Though CS_2 has been generally used as the solvent it is found that CH_2Cl_2 is more suitable in systems considered here. The products obtained from these reactions using CS_2 as solvent are often difficult to recrystallise.

In the benzoylation reaction of $CH_3C_5H_4Mn(CO)_3$, the acylium ion can attack one of the two possible positions of the $CH_3C_5H_4$ ring. When the substitution is at the α-position of the ring, the corresponding product formed is called an α-isomer. The β-isomer is formed likewise.

NMR spectral analyses show that the two isomers are formed in an almost 1:1 ratio. Apparently, there is no preferred site at which the acylium ion attacks.



The isomeric mixture obtained is usually a thick brown oil and does not readily crystallise out of solution. It has to be pumped at 50-60° for an hour in order to remove most of the unreacted starting materials and other volatile impurities. It is then extracted with petroleum ether (60-80°) and filtered (Fig. 2-1).

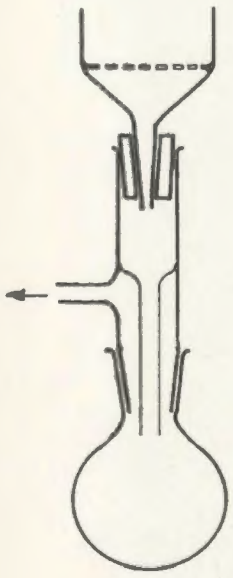


Fig. 2-1

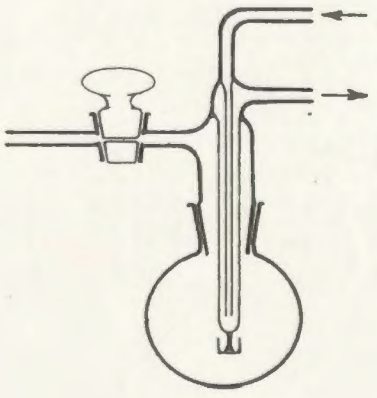


Fig. 2-2

The isomers are separated using one of the following techniques.

a) fractional recrystallisation.

b) column chromatography.

c) micro-distillation (Fig. 2-2).

d) preparation of derivatives.

The last method is used in cases where the isomers have very similar physical properties. For example, α-CH_3 and β-CH_3, $CH_3COC_5H_3Mn(CO)_3$ have been isolated by fractional recrystallisation of their corresponding oximes[5]. Subsequent hydrolyses of the oximes give the respective ketones.

Attempted preparation of o-methoxybenzoylcyclopentadienylmanganese tricarbonyl.

The difficulty encountered in the Friedel-Crafts aroylation using $o\text{-}CH_3OC_6H_4COCl$ and $C_5H_5Mn(CO)_3$ in the presence of $AlCl_3$ is because $AlCl_3$ is a good ether-cleaving agent[6]. At one stage of the experiment, the ortho hydroxy analogue was obtained. It is interesting to note, however, that the para methoxy analogue has been successfully prepared by this method.

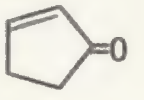
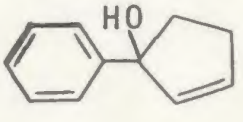
Attempts to prepare the ortho methoxy complex by treating the corresponding ortho halide complex with $NaOCH_3$ were not successful.

Preparation of phenylcyclopentadienylmanganese tricarbonyl.

This compound has been previously prepared by several workers. Brown and Shapiro[7] treated $MnBr_2$ with $Na^+C_5H_4$-$C_6H_5^-$ in THF and then subjected the product obtained to an atmosphere of CO at 210°/300 psi; Kozikowski and Larson[8] carbonylated $[C_6H_5C_5H_4]_2Mn$ with $Fe(CO)_5$ at 100°, and Pearson[9] electrolysed a mixture of MnI_2, $C_5H_5C_6H_5$ and $Mn_2(CO)_{10}$ under 800 atmospheres of CO. These methods are not very convenient and a less tedious method is therefore desirable. The following methods have been carried out but with little success.

$$\left.\begin{array}{l} C_6H_5MgBr + C_5H_5Mn(CO)_3 \not\longrightarrow \\ C_6H_5N_2^+Cl^- + C_5H_5Mn(CO)_3 \not\longrightarrow \\ C_6H_5^-Li^+ + C_5H_5Mn(CO)_3 \not\longrightarrow \end{array}\right\} C_6H_5C_5H_4Mn(CO)_3$$

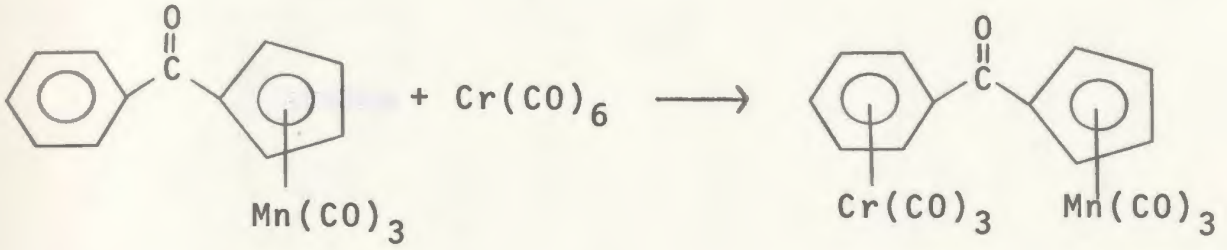
However, the method of phenylating 2-cyclopentene-1-one employed by Pauson[10] for the preparation of phenylcyclopentadiene proved successful.

$$C_6H_5^-Li^+ + \text{  } \longrightarrow \text{  } \xrightarrow{-H_2O} C_6H_5C_5H_5$$

$$C_6H_5C_5H_5 + Na \longrightarrow C_6H_5C_5H_4^-Na^+ \xrightarrow{Mn(CO)_5Br} C_6H_5C_5H_4Mn(CO)_3$$

Preparation of Tricarbonyl-π-chromium Complexes.

The aroylcyclopentadienylmanganese tricarbonyl can be π-complexed with a $Cr(CO)_3$ moiety by refluxing the former with excess $Cr(CO)_6$ in di-n-butyl ether[11,12] for about 6-10 hours.



The Soxhlet apparatus (Fig. 2-3) very conveniently allows the $Cr(CO)_6$ sublimate to be washed back into the reaction vessel. It is important that the whole system be carefully dried and flushed with dry N_2 before the freshly purified solvent and reagents are introduced into the reaction vessel. The reactions were carried out in the dark so as to prevent photochemical decomposition.

This method of preparing π-$Cr(CO)_3$ complexes has not been successfully used for these systems containing a halogen or a nitro group on the phenyl ring. It is not clear why chlorobenzene gives the corresponding π-$Cr(CO)_3$ complex[13] whereas attempts to prepare the corresponding π-complex of chlorobenzoylcyclopentadienylmanganese tricarbonyl have not been successful.

Several attempts have also been made to prepare π-$Mo(CO)_3$ complexes of these systems. Each attempt resulted in the quantitative recovery of the starting material. Apparently, the $Mo(CO)_3$ group does not seem to complex with these ligands as readily as the $Cr(CO)_3$ group. This may be attributed to both steric and stability factors.

EXPERIMENTAL

All the preparations were carried out in an inert atmosphere of dry N_2 which was purified by passing through Fieser's solution, lead acetate solution, sulfuric acid, soda lime and silica gel in that order.

The melting points were obtained from a Fisher-Johns block melting-point apparatus and the values quoted in the text are uncorrected.

The C, H and halogen analyses were carried out by Beller and Alfred Bernhardt Microanalytical Laboratories, W. Germany.

Metal Analyses were carried out with a Varian Model AA-5 Atomic Absorption Spectrophotometer.

The percentage yields are based on the metal-ligand carbonyls used.

Purification of Solvents.

All solvents were dried and distilled in an inert atmosphere of N_2 before use. Peroxides were removed from the di-n-butyl ether (Spectrograde; Matheson, Coleman and Bell) by shaking with a concentrated solution of ferrous sulphate. The ethereal layer was washed several times with water and dried over anhydrous $CaCl_2$. It was then refluxed over dispersed sodium in a stream of dry N_2 for an hour and a half before it was finally

collected at 141-142°.

Preparation of Manganese pentacarbonyl bromide, $Mn(CO)_5Br$.

10 g (0.026 m)* of resublimed $Mn_2(CO)_{10}$ (Pressure Chemical Co.) were dissolved in 400 ml of CCl_4 in a one litre three-neck flask fitted with a condenser and a N_2 inlet. The solution was stirred and 4.8 g (0.03 m) Br_2 dissolved in 100 ml CCl_4 were added dropwise. The mixture was stirred for two hours after which it was washed several times with water. The CCl_4 layer was dried over anhydrous $CaCl_2$. The resulting deep red solution was evaporated on a rotatory evaporator and the CCl_4 and excess Br_2 were removed. A yellow residue was obtained which was dried and sublimed at 55°/0.2 mm Hg (Yield 11.2 g, 78%).

Preparation of Bis-[manganese tetracarbonyl bromide], $[Mn(CO)_4Br]_2$.

The procedure was as described above except that the reaction mixture was heated to reflux. Highly insoluble crystalline copper-coloured flakes were obtained. This product was readily filtered and its purity checked with infrared and mass spectra (Yield 80%). It decomposed at about 290° without melting.

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*m = number of moles.

Preparation of Cyclopentadienylmanganese tricarbonyl, $C_5H_5Mn(CO)_3$.

Freshly distilled cyclopentadiene obtained from cracking di-cyclopentadiene was collected in a graduated vessel immersed in dry ice. 1.2 g (0.05 m) of dispersed sodium in THF were treated dropwise with 3.2 g (0.05 m) of cyclopentadiene dissolved in 50 ml of dry THF. Immediate effervescence was observed and the mixture was stirred for another hour. $[Mn(CO)_4Br]_2$, 11 g (0.02 m) was introduced into the reaction flask in the form of a slurry in THF. The mixture was refluxed for 3 hours. The flask was cooled and the solvent removed on a rotatory evaporator. The residue was extracted with CH_2Cl_2 and filtered. The filtrate was washed several times with water, dried over anhydrous $CaCl_2$ and the solvent removed. Yellow crystals were obtained which were resublimed twice. (Yield 6 g, 74%), mp 78-79° (lit.[14] 77°).

Preparation of Benzoylcyclopentadienylmanganese tricarbonyl, $C_6H_5COC_5H_4Mn(CO)_3$.
(Friedel-Crafts Benzoylation of $C_5H_5Mn(CO)_3$).

2 g (0.01 m) of resublimed $C_5H_5Mn(CO)_3$, were dissolved in 250 ml of dry CH_2Cl_2 in a 500 ml three-neck flask previously flushed with N_2. 1.4 g (0.01 m) of redistilled benzoyl chloride dissolved in 20 ml CH_2Cl_2

were added. Anhydrous $AlCl_3$ (Baker analysed reagent), 2 g (0.015 m) was immediately added into the reaction mixture and the latter allowed to warm slowly to reflux. The mixture turned dark red and was refluxed for 6-8 hours after which it was cooled to room temperature. Cold distilled water was added dropwise to destroy the aluminium complex. The CH_2Cl_2 layer was washed several times with water, dried over anhydrous $CaCl_2$ and the solvent removed. The resulting viscous orange liquid was pumped over a warm water bath, 50°/0.5 mm for half an hour. This liquid was then extracted with warm petroleum ether (60-80°) and filtered (Fig. 2-1). The filtrate was allowed to cool in the dark. Beautiful yellow crystals were obtained (Yield 2.4 g, 80%). It was recrystallised from petroleum ether; mp 73-74° (lit.[5] 73.5°).

Anal. Calc. for $C_{15}H_9O_4Mn$: C = 58.46; H = 2.94; Mn = 17.83.

Found: C = 58.28; H = 2.89; Mn = 18.02.

The following complexes have been prepared by the Friedel-Crafts reaction as described above.

Preparation of α- and β-Methyl, benzoylcyclopentadienyl-manganese tricarbonyl, $C_6H_5COC_5H_3(CH_3)Mn(CO)_3$.

The Friedel-Crafts reaction was carried out using

$CH_3C_5H_4Mn(CO)_3$ (Strem. Chemicals Inc.) in place of C_5H_5-$Mn(CO)_3$. The α- and β-isomers obtained were separated by fractional recrystallisation. Overall yield 76%. The more insoluble isomer was characterised by NMR spectral studies and found to be the α-isomer.

α-isomer mp 118-119° (lit.[5] 117-118°) ; β-isomer mp 54-55°.

Anal. Calc. for $C_{16}H_{11}MnO_4$: C = 59.64; H = 3.44; Mn = 17.06.

Found for α-isomer: C = 59.71; H = 3.39; Mn = 17.60.

Found for β-isomer: C = 59.85; H = 3.53; Mn = 17.62.

Preparation of o-Toluylcyclopentadienylmanganese tricarbonyl, $o\text{-}CH_3C_6H_4COC_5H_4Mn(CO)_3$.

Needle-shaped yellow crystals were obtained and recrystallised from petroleum ether. (Yield 70%) mp 108°.

Anal. Calc. for $C_{16}H_{11}MnO_4$: C = 59.64; H = 3.44; Mn = 17.06.

Found: C = 59.80; H = 2.88; Mn = 17.50.

Preparation of α- and β-Methyl, o-toluylcyclopentadienylmanganese tricarbonyl, $o\text{-}CH_3C_6H_4COC_5H_3(CH_3)Mn(CO)_3$.

The isomers were separated by eluting the mixture through a neutral alumina chromatographic column with a

80:20 mixture of petroleum ether/$CHCl_3$. The fractions were micro-distilled under reduced pressure (90-100°/0.2 mm Hg). (Overall yield 25%). The distillate obtained from the first fraction solidified as a yellow solid on the cold finger (Fig. 2-2). This was shown to be the α-isomer (mp 69-70°). The β-isomer remained as an oil and its purity was checked by its NMR spectrum and elemental analysis.

Anal. Calc. for $C_{17}H_{13}MnO_4$: C = 60.73; H = 3.90; Mn = 16.35.

Found for α-isomer: C = 60.82; H = 3.98; Mn = 16.58.

Found for β-isomer: C = 60.90; H = 3.68; Mn = 16.40.

Preparation of m-Toluylcyclopentadienylmanganese tricarbonyl, m-$CH_3C_6H_4COC_5H_3Mn(CO)_3$.

The orange liquid obtained was micro-distilled at 100°/0.4 mm Hg and then recrystallised from petroleum ether. (Yield 60%) mp 50°.

Anal. Calc. for $C_{16}H_{11}MnO_4$: C = 59.64; H = 3.44; Mn = 17.06.

Found: C = 60.04; H = 3.40; Mn = 17.13.

Preparation of α- and β-Methyl, m-toluylcyclopentadienylmanganese tricarbonyl, m-$CH_3C_6H_4COC_5H_3(CH_3)Mn(CO)_3$.

The β-isomer was obtained by cooling the ethereal

solution in dry ice and 'scratching' the walls of the container with a nickel spatula. It was recrystallised from petroleum ether twice to give beautiful rhombic--shaped yellow crystals. (Yield 55%) mp 66-67°.

Anal. Calc. for $C_{17}H_{13}MnO_4$: C = 60.73; H = 3.90; Mn = 16.35.

Found: C = 60.66; H = 3.86; Mn = 16.03.

The α-isomer has not been successfully isolated even after micro-distillation and eluting the distillate with heptane/$CHCl_3$ (70:30) over alumina. NMR spectral analysis showed the presence of about 5-10% of the β-isomer mixed with the α-isomer.

Preparation of p-Toluylcyclopentadienylmanganese tricarbonyl, p-$CH_3C_6H_4COC_5H_4Mn(CO)_3$.

Needle-shaped yellow crystals were obtained which were recrystallised from petroleum ether. (Yield 58%) mp 97°.

Anal. Calc. for $C_{16}H_{11}MnO_4$: C = 59.64; H = 3.44; Mn = 17.06.

Found: C = 59.56; H = 3.08; Mn = 17.21.

Preparation of α- and β-Methyl, p-toluylcyclopentadienylmanganese tricarbonyl, p-$CH_3C_6H_4COC_5H_3(CH_3)Mn(CO)_3$.

The isomers were separated by fractional recrystallisation. (Yield 80%). The more soluble yellow crystals

were shown to be the α-isomer.

α-isomer mp 96-97°; β-isomer mp 85°.

Anal. Calc. for $C_{17}H_{13}MnO_4$: C = 60.73; H = 3.90; Mn = 16.35.

Found for α-isomer: C = 61.00; H = 3.87; Mn = 16.21.

Found for β-isomer: C = 60.73; H = 3.97; Mn = 16.56.

Preparation of o-Chlorobenzoylcyclopentadienylmanganese tricarbonyl, o-$ClC_6H_4COC_5H_4Mn(CO)_3$.

Needle-shaped yellow crystals were obtained which were recrystallised from petroleum ether. (Yield 85%) mp 103-104°.

Anal. Calc. for $C_{15}H_8MnO_4Cl$: C = 52.58; H = 2.34; Mn = 16.03; Cl = 10.36.

Found: C = 52.44; H = 2.60; Mn = 15.96; Cl = 11.0.

Preparation of α- and β-Methyl, o-chlorobenzoylcyclopentadienylmanganese tricarbonyl, o-$ClC_6H_4COC_5H_3(CH_3)Mn(CO)_3$.

The isomers were isolated by fractional recrystallisation (Yield 65%). The more soluble yellow solid was found to be the β-isomer.

α-isomer mp 104-105°; β-isomer mp 70-71°.

Anal. Calc. for $C_{16}H_{10}MnO_4Cl$: C = 53.88; H = 2.83; Mn = 15.41; Cl = 9.95.

Found for α-isomer: C = 53.42; H = 2.91; Mn = 15.70; Cl = 10.11.

Found for β-isomer: C = 53.18; H = 2.94; Mn = 15.76; Cl = 10.33.

Preparation of p-Chlorobenzoylcyclopentadienylmanganese tricarbonyl, p-$ClC_6H_4COC_5H_4Mn(CO)_3$.

Monoclinic yellow crystals obtained which were recrystallised from petroleum ether. (Yield 65%) mp 85--86°.

Anal. Calc. for $C_{15}H_8MnO_4Cl$: C = 52.58; H = 2.34; Mn = 16.03; Cl = 10.36.

Found: C = 53.05; H = 2.36; Mn = 15.92; Cl = 10.49.

Preparation of α- and β-Methyl, p-chlorobenzoylcyclopentadienylmanganese tricarbonyl, p-$ClC_6H_4COC_5H_3(CH_3)Mn(CO)_3$.

The isomers were isolated by fractional recrystallisation (Yield 68%). The more soluble yellow crystals were shown to be the α-isomer.

α-isomer mp 72°; β-isomer mp 95°.

Anal. Calc. for $C_{16}H_{10}MnO_4Cl$: C = 53.88; H = 2.83; Mn = 15.41; Cl = 9.95.

Found for α-isomer: C = 53.56; H = 2.96; Mn = 14.98; Cl = 10.01.

Found for β-isomer: C = 53.32; H = 3.03; Mn = 15.90; Cl = 10.28.

Preparation of p-Fluorobenzoylcyclopentadienylmanganese tricarbonyl, p-$FC_6H_4COC_5H_4Mn(CO)_3$.

Monoclinic yellow crystals were obtained which were recrystallised from petroleum ether. (Yield 80%) mp 65°.

Anal. Calc. for $C_{15}H_8MnO_4F$: C = 55.24; H = 2.47; Mn = 16.84; F = 5.83.

Found: C = 54.95; H = 2.39; Mn = 16.64; F = 6.4.

Preparation of β-Methyl, p-fluorobenzoylcyclopentadienyl-manganese tricarbonyl, p-$FC_6H_4COC_5H_3(CH_3)Mn(CO)_3$.

The isomers were isolated by fractional recrystallisation (Yield 70%). The more soluble of the two was the α-isomer which was not isolated and remained as an oil.

β-isomer mp 67°.

Anal. Calc. for $C_{16}H_{10}MnO_4F$: C = 56.49; H = 2.96; Mn = 16.15; F = 5.59.

Found: C = 55.88; H = 2.98; Mn = 16.30; F = 5.8.

Preparation of m-Fluorobenzoylcyclopentadienylmanganese tricarbonyl, m-$FC_6H_4COC_5H_4Mn(CO)_3$.

Yellow crystals were obtained and were recrystallised from petroleum ether. (Yield 70%) mp 75°.

Anal. Calc. for $C_{15}H_8MnO_4F$: C = 55.24; H = 2.47; Mn = 16.84; F = 5.83.

Found: C = 55.41; H = 2.81; Mn = 17.10; F = 5.8.

Preparation of α- and β-Methyl, m-fluorobenzoylcyclopentadienylmanganese tricarbonyl, m-$FC_6H_4COC_5H_3(CH_3)Mn(CO)_3$.

Only the α-isomer was isolated (Yield 40%). It was recrystallised from petroleum ether. mp 113°.

Anal. Calc. for $C_{16}H_{10}MnO_4F$: C = 56.49; H = 2.96; Mn = 16.15; F = 5.59.

Found: C = 56.28; H = 2.75; Mn = 16.50; F = 5.6.

Preparation of o-Fluorobenzoylcyclopentadienylmanganese tricarbonyl, o-$FC_6H_4COC_5H_4Mn(CO)_3$.

Yellow crystals were obtained which were recrystallised from petroleum ether. (Yield 75%) mp 112°.

Anal. Calc. for $C_{15}H_8MnO_4F$: C = 55.24; H = 2.47; Mn = 16.84; F = 5.83.

Found: C = 55.44; H = 2.45; Mn = 16.28; F = 5.8.

Preparation of p-Methoxybenzoylcyclopentadienylmanganese tricarbonyl, p-$OCH_3C_6H_4COC_5H_4Mn(CO)_3$.

Yellow crystals were obtained and were recrystallised from petroleum ether. (Yield 60%) mp 92°.

Anal. Calc. for $C_{16}H_{11}O_5Mn$: C = 56.82; H = 3.28; Mn = 16.25.

Found: C = 56.91; H = 3.44; Mn = 16.17.

Preparation of α- and β-Methyl, p-methoxybenzoylcyclopentadienylmanganese tricarbonyl, $p\text{-}OCH_3C_6H_4COC_5H_3(CH_3)Mn(CO)_3$.

The isomers were isolated by fractional recrystallisation from petroleum ether (Yield 85%). The α-isomer was the more insoluble of the two.

α-isomer mp 103-104°; β-isomer mp 79-80°.

Anal. Calc. for $C_{17}H_{13}O_5Mn$: C = 57.97; H = 3.72; Mn = 15.60.

Found for α-isomer: C = 57.25; H = 3.85; Mn = 16.00.

Found for β-isomer: C = 56.88; H = 3.83; Mn = 15.90.

Preparation of α- and β-Methyl, acetylcyclopentadienylmanganese tricarbonyl, $CH_3COC_5H_3(CH_3)Mn(CO)_3$.

An orange liquid (4 g, 0.015 m) was obtained. This was dissolved in 50 ml of 95% EtOH and treated with a mixture of hydroxylamine hydrochloride (2 g, 0.029 m) and sodium acetate trihydrate (5 g, 0.04 m). The mixture was refluxed for 45 min, cooled and then poured into 200 ml of slightly acidified water. It was then extracted with benzene, dried over anhydrous Na_2SO_4 and filtered. The benzene was removed on a rotatory evaporator and petroleum ether (30-60°) was added. The solution was cooled in the dark and crystals were obtained. The corresponding α- and β-oximes were separated by fractional recrystallisation.

α-oxime mp 67-68° (lit.[5] 65-67°).

β-oxime mp 109-110° (lit.[5] 108°).

The oximes were then hydrolysed separately by refluxing with 20% H_2SO_4 in methanol. The solution was cooled, extracted with benzene, and then dried over anhydrous Na_2SO_4. The benzene was removed and the golden yellow liquid micro-distilled at 80°/0.2 mm Hg. The overall yield of both isomers was 50%. NMR spectra of these isomers showed that the separation was complete.

Preparation of Benzylcyclopentadienylmanganese tricarbonyl ketone, $C_6H_5CH_2COC_5H_4Mn(CO)_3$.

Purification was achieved by the chromatographic method using a 70:30 mixture of hexane/CH_2Cl_2 as eluant and alumina as the stationary phase. The yellow fraction obtained was micro-distilled (Fig. 2-2) and the viscous orange distillate crystallised on the cold-finger. (Yield 60%) mp 59°.

Anal. Calc. for $C_{16}H_{11}O_4Mn$: C = 59.64; H = 3.44; Mn = 17.06.

Found: C = 60.02; H = 3.52; Mn = 17.61.

Preparation of Benzylcyclopentadienylmanganese tricarbonyl methanol, $C_6H_5CH_2CH(OH)C_5H_4Mn(CO)_3$.

0.5 g (0.0016 m) of $C_6H_5CH_2COC_5H_4Mn(CO)_3$ was dissolved in 20 ml of absolute methanol and kept on a cold water bath at 20°. Sodium borohydride, 0.2 g (0.0053 m) dissolved

in 2 ml of 5%. NaOH was then slowly stirred into the reaction flask and the mixture was stirred in the cold bath for 2 hours. A small amount of the mixture was pipetted out and tested with dilute acid to ensure excess of borohydride. The methanol was distilled off and the resulting yellow solid was redissolved in diethyl ether. The ethereal solution was washed several times with water, dried over anhydrous $CaCl_2$ and the ether removed. Light-yellow solid (0.18 g, 90%) was obtained which was recrystallised from hot hexane mp 97°.

Anal. Calc. for $C_{16}H_{13}O_4Mn$: C = 59.27; H = 4.04; Mn = 16.95.

Found: C = 59.70; H = 3.98; Mn = 17.06.

Preparation of Styrylcyclopentadienylmanganese tricarbonyl, $C_6H_5CH{=}CHC_5H_4Mn(CO)_3$.

The freshly prepared $C_6H_5CH_2CH(OH)C_5H_4Mn(CO)_3$ (0.4 g, 0.001 m) was mixed with $KHSO_4$ (0.2 g, 0.0015 m) and a pinch of hydroquinone as catalyst. The mixture was heated in a stoppered flask equipped with a cold finger (Fig. 2-2) at a temperature of 170-175° for two hours. Droplets of water condensed on the cold finger. The residue was then micro-distilled and the distillate was collected at 100°/0.5 mm. The distillate solidified when disturbed (Yield 0.31 g, 82%) mp 97-98°.

Anal. Calc. for $C_{16}H_{11}O_3Mn$: C = 62.76; H = 3.62; Mn = 17.95.

Found: C = 62.66; H = 3.73; Mn = 18.02.

Preparation of α-Methyl, benzylcyclopentadienylmanganese tricarbonyl, $C_6H_5CH_2C_5H_3(\alpha\text{-}CH_3)Mn(CO)_3$.

A 1:1 mixture of $LiAlH_4$ (0.12 g, 0.003 m) and $AlCl_3$ (0.44 g, 0.003 m) in sodium-dried ether was treated dropwise with an ethereal solution of $C_6H_5COC_5H_3(\alpha\text{-}CH_3)Mn(CO)_3$ (1 g, 0.003 m). Brisk effervescence was observed and the solution turned from yellow to light red. The mixture was then refluxed for three hours, cooled in an ice-bath and then treated with water added dropwise. The ethereal layer was washed with a 5% solution of $NaHCO_3$ followed by water and then dried over anhydrous $MgSO_4$. The ether was removed on a rotatory evaporator and a viscous yellow oil was obtained. This was eluted with a 1:1 mixture of heptane/benzene over neutral alumina and two fractions were obtained. The first fraction was micro-distilled and the golden yellow distillate was collected at 110°/1 mm Hg (0.7 g, 76%). The second fraction was found to be the starting material. Infrared and NMR spectra confirmed the complete reduction of the ketonic carbonyl to the methylene group.

Anal. Calc. for $C_{16}H_{13}O_3Mn$: C = 62.35; H = 4.25; Mn = 17.83.

Found: C = 62.50; H = 4.01; Mn = 18.01.

Preparation of β-Methyl, benzylcyclopentadienylmanganese tricarbonyl, $C_6H_5CH_2C_5H_3(\beta\text{-}CH_3)Mn(CO)_3$.

The procedure was similar to that described above. The product was collected at 70°/1 mm (Yield 70%).

Preparation of Benzylcyclopentadienylmanganese tricarbonyl, $C_6H_5CH_2C_5H_4Mn(CO)_3$.

The reduction procedure was similar to that previously described. The product was collected as a golden yellow oil at 80°/0.2 mm which solidified when disturbed mechanically. (Yield 72%) mp 38°.

Anal. Calc. for $C_{15}H_{11}O_3Mn$: C = 61.24; H = 3.77; Mn = 18.68.

Found: C = 60.98; H = 3.70; Mn = 18.93.

Preparation of Pentadeuteriobenzoylcyclopentadienylmanganese tricarbonyl, $C_6D_5COC_5H_4Mn(CO)_3$.

20 g (0.12 m) of C_6D_5Br (Merck, Sharp and Dohme) were dissolved in 20 ml of anhydrous ether and slowly added to some magnesium turnings (3 g, 0.13 m). The Grignard reaction was initiated and allowed to react until all the C_6D_5Br was added. The mixture was refluxed for another hour. It was then poured into a beaker of solid CO_2 followed by 250 ml of 1:1 HCl which were slowly stirred

into the thick slurry. The mixture was extracted with ether and the combined ethereal solution was washed several times with water. 5% NaOH solution was used to extract the acid from the ethereal layer. The benzoic acid was precipitated out of solution with 1:1 HCl solution. This was filtered and dried over P_2O_5 (11.5 g, 76%). The NMR spectrum of this compound showed no indication of deuterium exchange.

The deuterated benzoic acid was treated with 15 g (0.12 m) of redistilled $SOCl_2$ in the presence of a trace of DMF and CuCl acting as a polymerisation inhibitor[15]. The mixture was placed over a hot water bath until no HCl or SO_2 was given off. Excess of $SOCl_2$ was distilled off and the C_6D_5COCl was collected at 100°/40 mm (10.8 g, 95%). The NMR spectrum confirmed the structure; no aromatic proton resonance was observed.

The C_6D_5COCl was then treated with $C_5H_5Mn(CO)_3$ and $AlCl_3$ as previously described in the Friedel-Crafts method of preparation. (Yield 56%) mp 134-135°.

Preparation of α- and β-Methyl, pentadeuteriobenzoylcyclopentadienylmanganese tricarbonyl, $C_6D_5COC_5H_3(CH_3)Mn(CO)_3$.

The preparation was carried out using Friedel-Crafts procedure. The isomers were isolated by fractional recrystallisation. NMR and mass spectral analyses showed

no detectable deuterium exchange. (Overall yield 65%).

α-isomer mp 121°; β-isomer mp 59-60°.

Preparation of Phenylcyclopentadienylmanganese tricarbonyl, $C_6H_5C_5H_4Mn(CO)_3$.

Phenyllithium was prepared by treating freshly cut lithium metal (1.5 g, 0.1 m) in di-ethyl ether with bromo-benzene (17.5 g, 0.1 m). The reaction was initiated by slow warming and then allowed to go to completion in an hour. The mixture was cooled and filtered on a vacuum line using Kontes "Airless ware apparatus". 5 g (0.06 m) of 2-cyclopentene-1-one dissolved in 20 ml ether were then slowly introduced into the phenyllithium. The mixture was stirred in an ice-bath for two hours, followed by another two hours at room temperature. It was then poured into a beaker of ice-cold water and the ethereal layer washed and dried over anhydrous $CaCl_2$. The ether was removed. The viscous oil obtained was dehydrated by blowing a stream of nitrogen over it at a temperature of about 180°. The dark yellow oil was distilled at 60-65°/ 0.3 mm and the clear distillate solidified as a white solid on the walls of the condenser. This solid readily changed to a light yellow oil on standing and had to be redistilled. (Yield 3.3 g, 40%) mp 47°. The mass-spectrum showed the molecular ion at m/e 142. The NMR spectrum showed peaks at 6.7 τ, 3.5τ, 3.2τ and 2.8τ

which agreed with that expected for monomeric $C_6H_5C_5H_5$.

The freshly prepared $C_6H_5C_5H_5$ (2.8 g, 0.01 m) was dissolved in 10 ml of THF and added slowly into a stirred mixture of dispersed sodium (0.46 g, 0.02 m) in THF. The mixture was refluxed for an hour, cooled and 2.7 g (0.01 m) of $Mn(CO)_5Br$ dissolved in THF were added dropwise. It was then refluxed for another two hours. The excess sodium was destroyed using aqueous pet-ether (30--60°). The ethereal layer was washed several times with water and dried over anhydrous $CaCl_2$. The ether was removed and the resulting viscous oil distilled. Clear golden yellow oil droplets were collected at 65--70°/0.3 mm (Yield 0.84 g, 40%).

Anal. Calc. for $C_{14}H_9O_3Mn$: C = 60.02; H = 3.24; Mn = 19.62.

Found: C = 60.84; H = 3.41; Mn = 19.71.

Preparation of (Tricarbonyl-π-chromium)benzoylcyclopentadienylmanganese tricarbonyl, $[(CO)_3Cr]C_6H_5COC_5H_4Mn(CO)_3$.

A mixture of $C_6H_5COC_5H_4Mn(CO)_3$ (0.6 g, 0.002 m) and resublimed $Cr(CO)_6$ (0.5 g, 0.003 m) (Pressure Chemical Co.) was placed in the thimble and the set-up (Fig. 2-3) was carefully flushed with dry N_2. 20 ml of degassed di-n-butyl ether were introduced into the flask equipped with a magnetic stirrer. The ether was slowly heated to

reflux. The condensed ether in the Soxhlet washed part of the mixture down from the thimble to the reaction flask. This process was allowed to continue in the dark for 8 hours until the mixture turned reddish orange. It was then cooled to about 100°, filtered hot and the ether removed on a rotatory evaporator under reduced pressure. The excess $Cr(CO)_6$ was also removed during this process. The reddish orange crystals obtained were extracted with hot petroleum ether, filtered and allowed to cool in the dark. Red crystals were obtained (Yield 0.48 g, 49%) mp 133-134°.

Anal. Calc. for $C_{18}H_9O_7MnCr$: C = 48.67; H = 2.04; Mn = 12.37; Cr = 11.71.

Found: C = 49.20; H = 1.96; Mn = 13.00; Cr = 11.96.

The analogous deuterated benzoyl complex was similarly prepared (Yield 65%) mp 133-135°.

The following complexes have been prepared by the procedure just described.

Preparation of α-Methyl, (tricarbonyl-π-chromium)benzoylcyclopentadienylmanganese tricarbonyl, $[(CO)_3Cr]C_6H_5COC_5H_3(\alpha\text{-}CH_3)Mn(CO)_3$.

An orange solid was obtained. This product was recrystallised with petroleum ether in a Soxhlet extractor. The ether solution, on cooling in the dark overnight, gave bright red crystals. (Yield 47%) mp 132°.

Anal. Calc. for $C_{19}H_{11}O_7MnCr$: C = 49.80; H = 2.42; Mn = 11.99; Cr = 11.35.

Found: C = 50.01; H = 2.38; Mn = 12.36; Cr = 11.65.

The analogous deuterated-benzoyl complex was similarly prepared (Yield 60%) mp 136-137°.

Preparation of β-Methyl, (tricarbonyl-π-chromium)benzoylcyclopentadienylmanganese tricarbonyl, $[(CO)_3Cr]C_6H_5COC_5H_3(\beta\text{-}CH_3)Mn(CO)_3$.

The reddish orange solid obtained was recrystallised from petroleum ether in a Soxhlet extractor. This gave bright red crystals (Yield 56%) mp 128° (decomp.).

Anal. Calc. for $C_{19}H_{11}O_7MnCr$: C = 49.80; H = 2.42; Mn = 11.99; Cr = 11.35.

Found: C = 50.10; H = 2.36; Mn = 12.16; Cr = 11.60.

The analogous deuterated-benzoyl complex was similarly prepared (Yield 58%) mp 132° (decomp.).

Preparation of (Tricarbonyl-π-chromium)o-toluylcyclopentadienylmanganese tricarbonyl, $[(CO)_3Cr]o\text{-}CH_3C_6H_4COC_5H_4Mn(CO)_3$.

Monoclinic yellow crystals were obtained after recrystallisation from petroleum ether (Yield 75%) mp 147-149° (decomp.).

Anal. Calc. for $C_{19}H_{11}O_7MnCr$: C = 49.80; H = 2.42; Mn = 11.99; Cr = 11.35.

Found: C = 50.00; H = 2.34; Mn = 12.16; Cr = 11.54.

Preparation of α-Methyl, (tricarbonyl-π-chromium)o-toluyl-cyclopentadienylmanganese tricarbonyl, $[(CO)_3Cr]o\text{-}CH_3C_6H_4\text{-}COC_5H_3(\alpha\text{-}CH_3)Mn(CO)_3$.

The crystals obtained from recrystallisation with petroleum ether were of two physical forms; a light yellow powder (mp 167-168°) and orange crystals (mp 158-160°). These were separated mechanically. Infrared and NMR studies suggest that they are rotational isomers (Yield 60%).

Anal. Calc. for $C_{20}H_{13}O_7MnCr$: C = 50.87; H = 2.77; Mn = 11.63; Cr = 11.02.

Found: C = 51.16; H = 2.90; Mn = 11.53; Cr = 11.51.

Preparation of β-Methyl, (tricarbonyl-π-chromium)o-toluyl-cyclopentadienylmanganese tricarbonyl, $[(CO)_3Cr]o\text{-}CH_3C_6H_4\text{-}COC_5H_3(\beta\text{-}CH_3)Mn(CO)_3$.

Bright yellow crystals were obtained which were re-crystallised from petroleum ether (Yield 68%) mp 104-106°.

Anal. Calc. for $C_{20}H_{13}O_7MnCr$: C = 50.87; H = 2.77; Mn = 11.63; Cr = 11.02.

Found: C = 51.00; H = 2.51; Mn = 11.86; Cr = 11.00.

Preparation of (Tricarbonyl-π-chromium)m-toluylcyclopentadienylmanganese tricarbonyl, $[(CO)_3Cr]m\text{-}CH_3C_6H_4COC_5H_4Mn(CO)_3$.

An orange oil was obtained which did not crystallise out of petroleum ether even under forced precipitation conditions. It was then chromatographed in the dark using a 2:1 mixture of pet-ether/$CHCl_3$ eluted over alumina. The ethereal solution was allowed to cool in the dark for several days. Red crystals were obtained (Yield 60%) mp 94-95°.

Anal. Calc. for $C_{19}H_{11}O_7MnCr$: C = 49.80; H = 2.42; Mn = 11.99; Cr = 11.35.

Found: C = 49.82; H = 2.56; Mn = 12.37; Cr = 11.85.

Preparation of β-Methyl, (tricarbonyl-π-chromium)m-toluylcyclopentadienylmanganese tricarbonyl, $[(CO)_3Cr]m\text{-}CH_3C_6H_4\text{-}COC_5H_3(\beta\text{-}CH_3)Mn\ (CO)_3$.

A reddish orange oil was obtained and was similarly purified by the method previously described. Red needle-shaped crystals were obtained (Yield 70%) mp 94-95°.

Anal. Calc. for $C_{20}H_{13}O_7MnCr$: C = 50.87; H = 2.77; Mn = 11.63; Cr = 11.02.

Found: C = 51.04; H = 2.86; Mn = 11.82; Cr = 11.35.

Preparation of (Tricarbonyl-π-chromium)p-toluylcyclopentadienylmanganese tricarbonyl, $[(CO)_3Cr]p\text{-}CH_3C_6H_4COC_5H_4Mn(CO)_3$.

Beautiful orange monoclinic crystals were obtained

from recrystallisation with petroleum ether. (Yield 60%) mp 126°.

Anal. Calc. for $C_{19}H_{11}O_7MnCr$: C = 49.80; H = 2.42; Mn = 11.99; Cr = 11.35.

Found: C = 49.90; H = 2.21; Mn = 12.02; Cr = 11.76.

Preparation of α-Methyl, (tricarbonyl-π-chromium)p-toluyl-cyclopentadienylmanganese tricarbonyl, $[(CO)_3Cr]p\text{-}CH_3C_6H_4\text{-}COC_5H_3(\alpha\text{-}CH_3)Mn(CO)_3$.

Bright red crystals were obtained from recrystallisation with petroleum ether (Yield 77%) mp 113°.

Anal. Calc. for $C_{20}H_{13}O_7MnCr$: C = 50.87; H = 2.77; Mn = 11.63; Cr = 11.02.

Found: C = 50.80; H = 2.92; Mn = 12.12; Cr = 11.24.

Preparation of β-Methyl, (tricarbonyl-π-chromium)p-toluyl-cyclopentadienylmanganese tricarbonyl, $[(CO)_3Cr]p\text{-}CH_3C_6H_4\text{-}COC_5H_3(\beta\text{-}CH_3)Mn(CO)_3$.

Reddish orange crystals were obtained after several recrystallisations from petroleum ether. (Yield 80%) mp 150°.

Anal. Calc. for $C_{20}H_{13}O_7MnCr$: C = 50.87; H = 2.77; Mn = 11.63; Cr = 11.02.

Found: C = 50.83; H = 2.86; Mn = 11.82; Cr = 11.31.

Preparation of (Tricarbonyl-π-chromium)p-methoxybenzoyl-cyclopentadienylmanganese tricarbonyl, $[(CO)_3Cr]p\text{-}OCH_3C_6H_4\text{-}COC_5H_4Mn(CO)_3$.

A dirty orange solid was first obtained. It was dissolved in a 1:2 mixture of $CHCl_3$/pet-ether and filtered. The clear filtrate was placed over a rotatory evaporator and part of the $CHCl_3$ was removed. The enriched petroleum ether solution was cooled in the dark. Fine orange crystals were obtained (Yield 85%) mp 154°.

Anal. Calc. for $C_{19}H_{11}O_8MnCr$: C = 48.12; H = 2.34; Mn = 11.58; Cr = 10.97.

Found: C = 48.19; H = 2.61; Mn = 11.54; Cr = 11.16.

Preparation of α-Methyl, (tricarbonyl-π-chromium)p-methoxybenzoylcyclopentadienylmanganese tricarbonyl, $[(CO)_3Cr]p\text{-}\text{-}OCH_3C_6H_4COC_5H_3(\alpha\text{-}CH_3)Mn(CO)_3$.

The dirty orange product was purified by the method described above. (Yield 78%) mp 133-134°.

Anal. Calc. for $C_{20}H_{13}O_8MnCr$: C = 49.20; H = 2.68; Mn = 11.25; Cr = 10.66.

Found: C = 49.16; H = 2.76; Mn = 11.53; Cr = 10.21.

Preparation of β-Methyl, (tricarbonyl-π-chromium)p-methoxybenzoylcyclopentadienylmanganese tricarbonyl, $[(CO)_3Cr]\text{-}p\text{-}OCH_3C_6H_4COC_5H_3(\beta\text{-}CH_3)Mn(CO)_3$

The crude product was purified by the method described

above. Orange crystals were obtained (Yield 75%) mp 136°.

Anal. Calc. for $C_{20}H_{13}O_8MnCr$: C = 49.20; H = 2.68; Mn = 11.25; Cr = 10.66.

Found: C = 47.98; H = 2.62; Mn = 10.99; Cr = 10.18.

Preparation of (Tricarbonyl-π-chromium)phenylcyclopentadienylmanganese tricarbonyl, $[(CO)_3Cr]C_6H_5C_5H_4Mn(CO)_3$.

The yellow solid obtained after 50 hours reflux was purified with petroleum ether in a Soxhlet extractor. Yellow crystals were obtained on cooling (Yield 50%) mp 156-157° (decomp.).

Anal. Calc. for $C_{17}H_9O_6MnCr$: C = 49.06; H = 2.18; Mn = 13.21; Cr = 12.50.

Found: C = 49.10; H = 2.22; Mn = 13.60; Cr = 12.90.

Preparation of (Tricarbonyl-π-chromium)benzylcyclopentadienylmanganese tricarbonyl, $[(CO)_3Cr]C_6H_5CH_2C_5H_4Mn(CO)_3$.

Greenish yellow crystals were obtained which were recrystallised from petroleum ether (Yield 40%) mp 106--107°.

Anal. Calc. for $C_{18}H_{11}O_6CrMn$: C = 50.25; H = 2.58; Mn = 12.77; Cr = 12.09.

Found: C = 50.23; H = 2.58; Mn = 12.78; Cr = 12.10.

Preparation of α-Methyl, (tricarbonyl-π-chromium)benzylcyclopentadienylmanganese tricarbonyl, $[(CO)_3Cr]C_6H_5CH_2$-$C_5H_3(\alpha\text{-}CH_3)Mn(CO)_3$.

Greenish yellow crystals were obtained which were recrystallised from petroleum ether (Yield 70%) mp 113--114°.

Anal. Calc. for $C_{19}H_{13}O_6CrMn$: C = 51.37; H = 2.95; Mn = 12.37; Cr = 11.71.

Found: C = 51.60; H = 2.75; Mn = 12.76; Cr = 12.00.

Preparation of β-Methyl, (tricarbonyl-π-chromium)benzylcyclopentadienylmanganese tricarbonyl, $[(CO)_3Cr]C_6H_5CH_2$-$C_5H_3(\beta\text{-}CH_3)Mn(CO)_3$.

Yellow crystals were obtained which were recrystallised from petroleum ether (Yield 80%) mp 98-99°.

Anal. Calc. for $C_{19}H_{13}O_6CrMn$: C = 51.37; H = 2.95; Mn = 12.37; Cr = 11.71.

Found: C = 51.78; H = 2.57; Mn = 12.84; Cr = 11.83.

Preparation of (Tricarbonyl-π-chromium)benzylcyclopentadienylmanganese tricarbonyl ketone, $[(CO)_3Cr]C_6H_5CH_2CO$-$C_5H_4Mn(CO)_3$.

A greenish yellow solid was obtained which was very insoluble in petroleum ether. It readily decomposed in halogenated hydrocarbons like $CHCl_3$, CH_2Cl_2 and CCl_4.

It was purified with petroleum ether using a Soxhlet extractor and in the dark. Light greenish-yellow crystals were obtained (Yield 56%) mp 129-130° (decomp.).

Anal. Calc. for $C_{19}H_{11}O_7MnCr$: C = 49.80; H = 2.42; Mn = 11.99; Cr = 11.35.

Found: C = 50.00; H = 2.52; Mn = 12.06; Cr = 11.67.

Preparation of (Tricarbonyl-π-chromium)benzylcyclopentadienylmanganese tricarbonyl methanol, $[(CO)_3Cr]C_6H_5CH_2CH(OH)C_5H_4Mn(CO)_3$.

Yellow crystals were obtained which were recrystallised from 1:3 mixture of CCl_4/pet-ether (Yield 76%) mp 132-133°.

Anal. Calc. for $C_{19}H_{13}O_7MnCr$: C = 49.58; H = 2.85; Mn = 11.94; Cr = 11.30.

Found: C = 49.64; H = 2.92; Mn = 12.02; Cr = 11.58.

Preparation of (Tricarbonyl-π-chromium)styrylcyclopentadienylmanganese tricarbonyl, $[(CO)_3Cr]C_6H_5CH=CHC_5H_4Mn(CO)_3$.

The crude yellow product was recrystallised from a mixture of 2:3 CH_2Cl_2/pet-ether. Light yellowish-orange crystals were obtained on cooling (Yield 80%) mp 157° (decomp.).

Anal. Calc. for $C_{19}H_{11}O_6MnCr$: C = 51.60; H = 2.51; Mn = 12.43; Cr = 11.76.

Found: C = 51.85; H = 2.62; Mn = 12.80; Cr = 12.00.

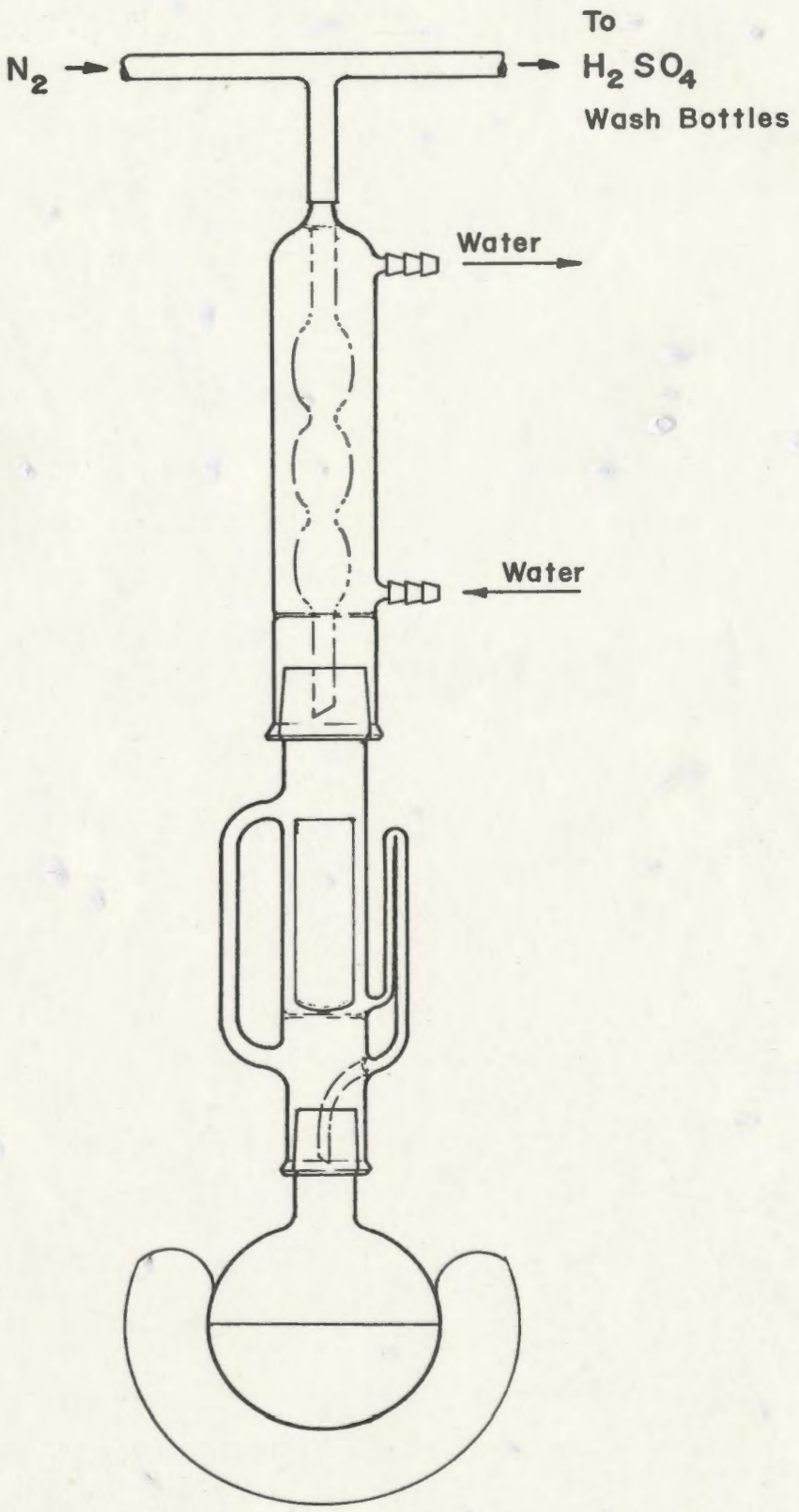

Fig. 2-3

Soxhlet Extractor Set-up For Preparing π-$Cr(CO)_3$ Complexes

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CHAPTER 3

INFRARED STUDIES

INTRODUCTION

Ring Vibrational Modes:

The infrared spectrum of the much celebrated metallo-cyclopentadienyl compound $(C_5H_5)_2Fe$, was first studied by Lippincott and Nelson[1]. They assumed that interactions between the two rings were negligible and that the D_{5d} symmetry could be considered as comprising two local C_{5v} point-groups. Apart from the two vibrational modes involving ring-metal stretch and ring tilt, all other ring modes were essentially those of unperturbed C_5H_5. In this way they have been able to assign tentatively the various vibrational ring modes.

This study was extended to half-sandwich complexes such as $C_5H_5Mn(CO)_3$. Micro-wave[2] and X-ray[3] studies showed that the C_5H_5 ring could be regarded as having a local C_{5v} symmetry and the $Mn(CO)_3$ group as having an independent C_{3v} symmetry. As such the C_5H_5 ring modes could be correlated with those of ferrocene. Fritz[4] has assigned the ring stretching frequencies for $C_5H_5Mn(CO)_3$ and similar work has been carried out by Lippincott et al.[5] and Stiddard et al.[6]. The latter workers extended their work to $CH_3C_5H_4Mn(CO)_3$ where they compared the spectrum

of this compound with that of $C_5H_5Mn(CO)_3$ in a way similar to the comparison of the spectra of toluene and benzene[7].

No such comparative studies have been done for bis-π-benzenechromium and π-benzenechromium tricarbonyl. Probably the benzene ring in the latter resembles benzene itself more than that of the former. Furthermore, bis-π-benzenechromium is known to have considerable metal-ligand interaction[8]. Fritz and Manchot[9,10] made a detailed study of $C_6H_6M(CO)_3$, where M = Cr or Mo, and the corresponding deuterated compounds. The vibrations, however, were reassigned by Adams and Squire[11] who suggested that the symmetry of the benzene ring is reduced from D_{6h} to C_{3v}.

$M(CO)_3$ Vibrational Modes:

The carbonyl stretching frequencies of $M(CO)_6$ differ from those of half-sandwich complexes in that the ring is capable of donating charge to the metal. This in turn is transferred to the carbonyls rendering the M-CO bond stronger and the C-O bond weaker as compared to those of $M(CO)_6$ (Table 3-1)[12]. Table 3-1 also shows that an electron donating substituent like NH_2 increases the charge transfer from the ring to the metal. This further increases the M-CO bond order and at the same time reduces the bond

order of C-O relative to the unsubstituted complex.

TABLE 3-1[12]

Molecule	k_{C-O} (mdynes/Å)	C-O overlap population	Cr-CO overlap population
CO	18.53	1.385	---
$Cr(CO)_6$	16.49	1.317	0.415
$C_6H_6Cr(CO)_3$	11.95	1.216	0.537
$NH_2C_6H_5Cr(CO)_3$	11.76	1.212	0.540

Brown and co-workers[13] have carried out some molecular orbital calculations employing the Self-Consistent Charge Method (SCCC), on hexacarbonyls of Cr, Mo and W. They extended the calculations to include π-arenechromium tricarbonyl derivatives and obtained some good correlations between calculated energy levels and overlap populations and observed properties such as ionisation potentials, infrared frequencies, and solvent effects[13]. The success of these results lends credence to Kettle's[15,16] theoretical argument that the π-overlap integral $2p\pi 2p\pi$(C-O), is more affected than the corresponding σ-overlap integral when the C-O bond distance of metal carbonyls is varied.

Brown and Carroll[14] observed that the ring-Cr-C deformation bands in $C_6H_5XCr(CO)_3$ are insensitive to

substituent effects and no correlations are obtained for X = Cl, H, CH_3, NH_2, NHMe and NMe_2 in the low frequency region. Significant shifts are, however, observed in the A_1 and E modes of the CO stretching frequencies. It is concluded that the π-electron effects of substituents are more strongly transmitted from the arene ring to the metal atom than their inductive effects. This conclusion is questionable since it is based on comparison of vibrational modes in the low frequency region which have not been unambiguously assigned.

The most important and widely used approximation method for these half-sandwich complexes is the concept of local symmetry. Adams and Squire[11] have shown that such an approximation is valid for solution spectra but inadequate for solid state spectra of mono-substituted ring ligands. For more complex molecules it is necessary to consider the factor group analysis[17]. In any case, it is assumed that $M(CO)_3$ has C_{3v} local symmetry and the number of normal modes to be expected is 3N-6. This is spanned by the representations $4A_1 + A_2 + 5E$. By choosing the appropriate sets of internal displacement co-ordinates and performing symmetry operations as required, the following representations can be deduced:

C=O	stretching modes	$A_1 + E$
M-CO	stretching modes	$A_1 + E$
C-M-C	angle deformation	$A_1 + E$
M-C-O	angle deformation	$A_1 + A_2 + 2E$

A pure C≡O bond is much stronger than the M-C bond. Its stretching frequencies are very much higher than those of the skeletal fundamentals of these molecules. It is therefore justifiable to assume that there are no significant interactions between the CO stretching frequencies and other vibrations in the molecule.

The vibrational modes of $C_5H_5Mn(CO)_3$ and π-arene-chromium tricarbonyls have been tentatively assigned by a number of workers[5,6,18,19] but they are still under constant review with the advent of more sophisticated instruments and techniques. Generally the non-ring modes can be summarised as follows:

1) The C-M-C angle deformations occur near 100 cm^{-1}
2) M-C stretching vibrations are rarely above 500 cm^{-1}
3) M-C-O angle deformations are sensitive to their environment and can be anywhere between 735 and 275 cm^{-1}.

Table 3-2 shows the assignments for non-ring modes of $C_6H_6Cr(CO)_3$ and $C_5H_5Mn(CO)_3$ obtained by Fritz and Manchot[9]. The values within brackets are those assigned by Lippincott et al.[5].

Butler and Fenster[20] have carried out labelling studies using ^{13}CO and $C^{18}O$ in some π-cyclopentadienylmanganese tricarbonyl complexes and demonstrated that the method of local

symmetry can be used to predict the infrared spectra of these complexes. Haas and Sheline[21], and Cotton and Kraihanzel[22] were able to relate observed CO stretching vibrations with calculated force constants. Though many crude approximations are made, the results are nevertheless very useful in assigning C-O vibrational frequencies.

TABLE 3-2[5]

Non-Ring Modes of $C_6H_6Cr(CO)_3$ and $C_5H_5Mn(CO)_3$

Mode	Symmetry	$C_6H_6Cr(CO)_3$ (cm^{-1})	$C_5H_5Mn(CO)_3$ (cm^{-1})
νR-M	A_1	298	350
Twist R-M-C	A_1	not observed	160
Ring tilt	E	330	375
δR-M-C	E	not observed	100 or 120
νM-C	A_1	535 (483)	500
νM-C	E	306	480
δC-M-C	A_1	483	140
δC-M-C	E	not observed	120 or 100
νCO	A_1	2005	2025
νCO	E	1946	1940
δM-C-O	A_1	664	540
δM-C-O	A_2	not observed	610
δM-C-O	E	633	635
δM-C-O	E	not observed (535)	670, 665

(R = ring, M = metal, ν = stretching vibration, δ = bending deformation)

Solvent effects and relative intensity studies of a series of substituted arene complexes of Cr, Mo and W tricarbonyls were carried out by Brown and Hughes[23]. They concluded that the greater the solvent-induced shift, the lower the ν(CO) frequencies and subsequently the more the π- character in the M-CO bond. It was observed that the solvent shifts decreased in the order W > Mo > Cr implying that the $d\pi$-$p\pi$ interactions of metal-CO decreased in the order W-CO > Mo-CO > Cr-CO.

RESULTS AND DISCUSSION

Though many infrared studies had been carried out on systems like $C_5H_5Mn(CO)_3$ and $C_6H_6Cr(CO)_3$, no similar studies have been attempted on systems in which both these moieties are combined.

In this study the systems shown in Fig. 3-1 where X = H, CH_3, OCH_3, Cl, F and Y = H or CH_3 were investigated.

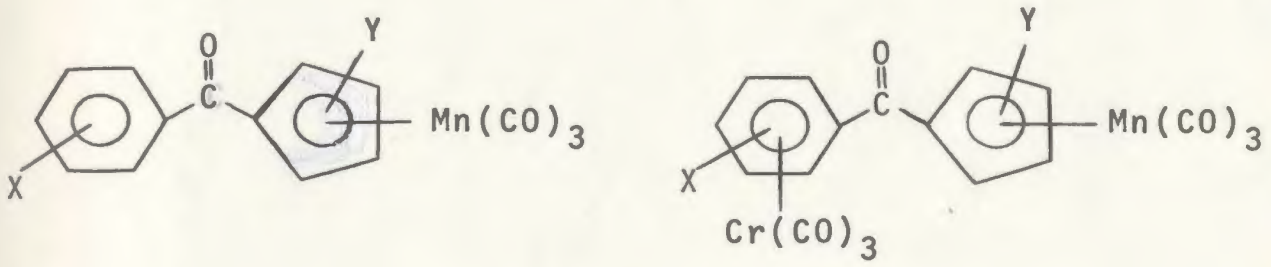


Fig. 3-1

Since the $M(CO)_3$ moieties in $C_5H_5Mn(CO)_3$ and $C_6H_6Cr(CO)_3$ are isostructural their spectra in the region of δ(M-C-O) and ν(M-CO) modes are very similar as evident from Table 3-2. It is rather tedious and complicated to assign unambiguously the various vibrational bands except those of carbonyl stretching frequencies of the metal CO and ketonic CO. These large molecules, strictly speaking have symmetry C_s. However, an approximate C_{3v} local symmetry can be assumed for $M(CO)_3$ in the discussion of their solution spectra.

Carbonyl Vibrational Modes:

Table 3-3 shows the A_1 and E carbonyl stretching modes of some derivatives of $C_5H_5Mn(CO)_3$. When the cyclopentadienyl ring is substituted with a methyl group there is a general decrease in the C-O stretching frequencies of the $Mn(CO)_3$ moiety. Though this decrease is small, it is nevertheless consistently recurring as observed in Fig. 3-2. This is in agreement with simple molecular orbital theory as discussed by Brown and Sloan.[24] The electron donating substituent enhances the ($a_1$4s/4p) interaction of the ligand with metal which results in an increase in charge-transfer to the central metal atom. Subsequent increase in the negative charge on the metal leads to a greater transfer of charge to the vacant orbitals of the carbonyl groups, hence lowering the C-O stretching frequencies. In simple resonance terminology, an electron donating substituent X will prefer the canonical structure II to I.

$$X\text{-}C_5H_4\text{—}Mn\text{—}C\equiv O \longleftrightarrow X^{+}C_5H_4\text{=}Mn\text{=}C\text{=}O^{-}$$

(I) (II)

Corresponding increases in the M-C stretching and M-C-O deformation frequencies are expected. However, such changes are difficult to detect because these modes are not sensitive to substituent changes. Furthermore, they have not been unambiguously assigned.

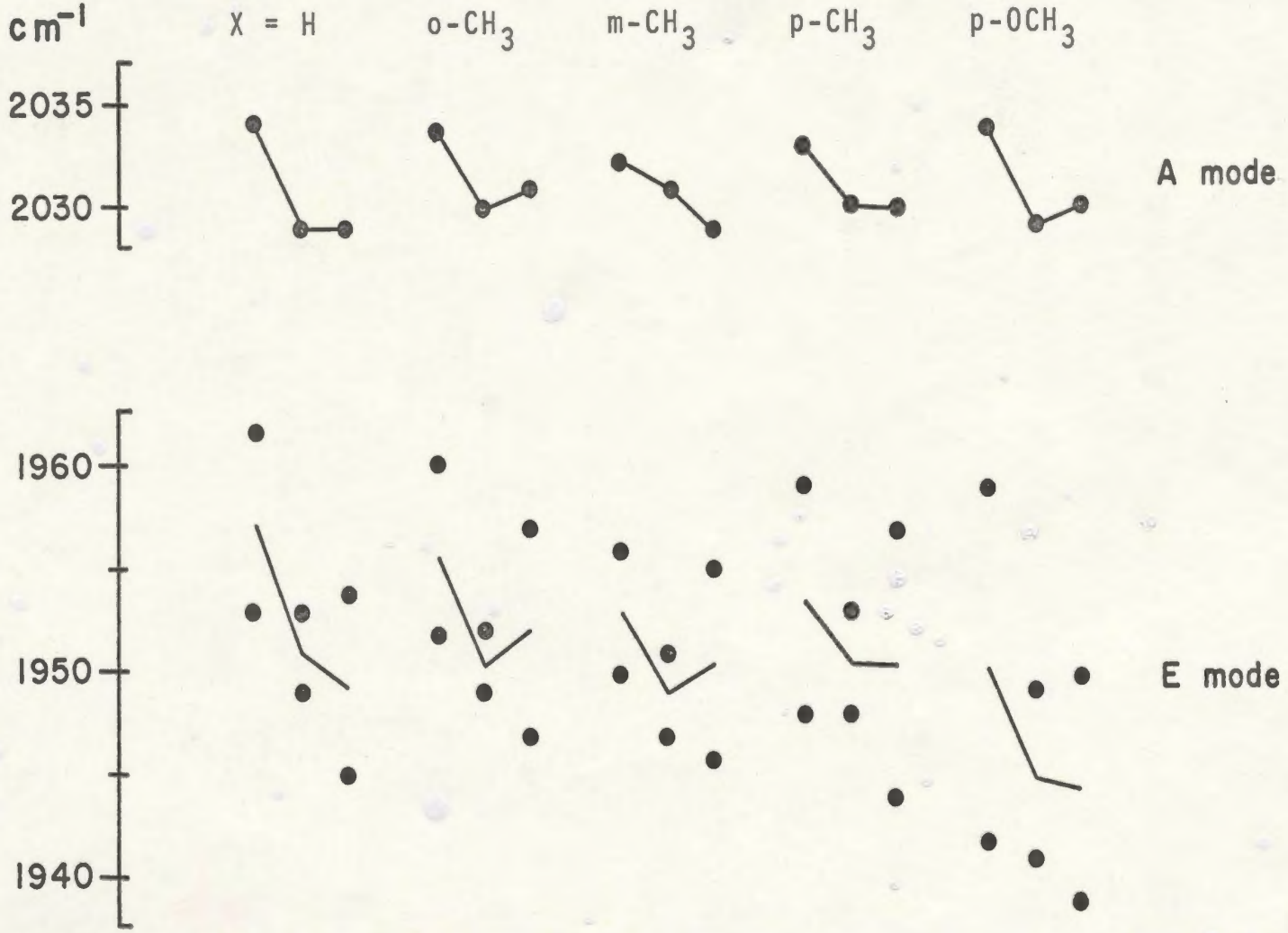
TABLE 3-3

Carbonyl Stretching Frequencies of Some $X\text{-}C_6H_4COC_5H_3YMn(CO)_3$ Compounds (cm^{-1})

	Y = H		ketonic	Y = α-CH_3		ketonic	Y = β-CH_3		ketonic
X	A_1	E	ν(C-O)	A_1	E	ν(C-O)	A_1	E	ν(C-O)
H-	2034	1962,1953	1661	2029	1953,1949	1659	2030	1954,1945	1659
o-CH_3-	2034	1960,1952	1665	2030	1952,1949	1662	2031	1957,1947	1665
m-CH_3-	2032	1956,1950	1655	2031	1951,1947	1653	2029	1955,1946	1655
p-CH_3-	2033	1959,1948	1655	2033	1953,1948	1656	2030	1957,1944	1655
p-OCH_3-	2034	1959,1947	1649	2029	1953,1946	1650	2030	1955,1946	1648
o-Cl-	2034	1958,1952	1673	2031	1948,1950	1663	2031	1955,1947	1669
p-Cl-	2031	1961,1952	1657	2029	1955,1950	1660	2028	1959,1948	1656
o-F-	2032	1963,1954	1666	-	-	-	-	-	-
m-F-	2032	1960,1951	1660	2030	1954,1951	1660	-	-	-
p-F-	2034	1960,1951	1656	-	-	-	2028	1955,1946	1655

Fig. 3-2

Effects of Methyl Substituent at Cyclopentadienyl Ring on the CO vibrations of $Mn(CO)_3$ in $XC_6H_4COC_5H_3YMn(CO)_3$



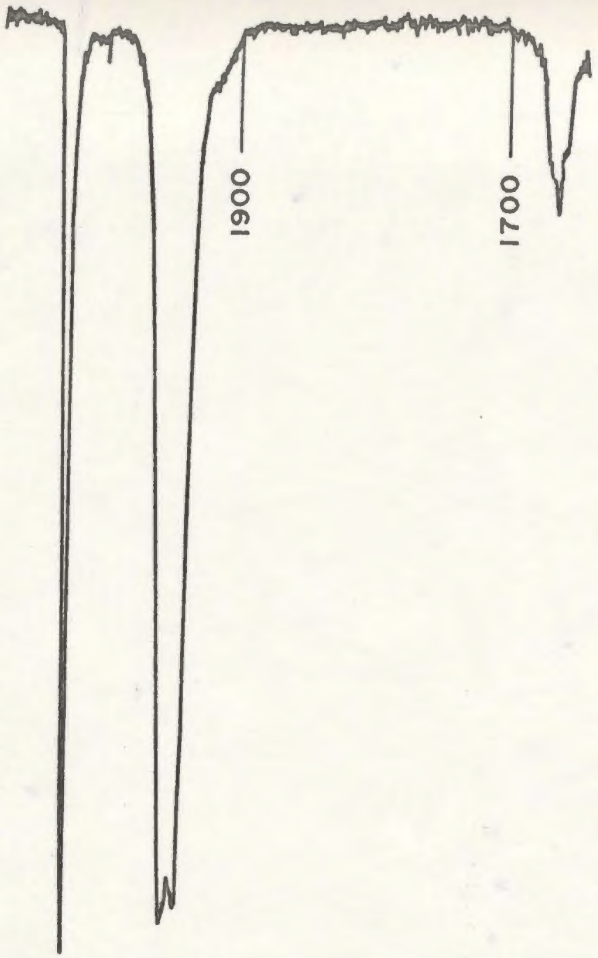
(The triads are of the order Y = H, Y = α-CH_3, Y = β-CH_3 respectively)

Table 3-3 shows that substituents on the phenyl rings are too remote to have any electronic effects on the $Mn(CO)_3$ moiety. Only a random change in the C-O stretching vibrations is observed. This does not imply that the two ring systems are not conjugated. Perhaps this conjugation is not as strong as in biphenyl or phenanthrene derivatives[25] where the ring systems are directly linked to each other and substituent changes on one ring effect the C-O vibrations of the $M(CO)_3$ complexed to the other.

Carbonyl Vibrations of $Cr(CO)_3$ moiety:

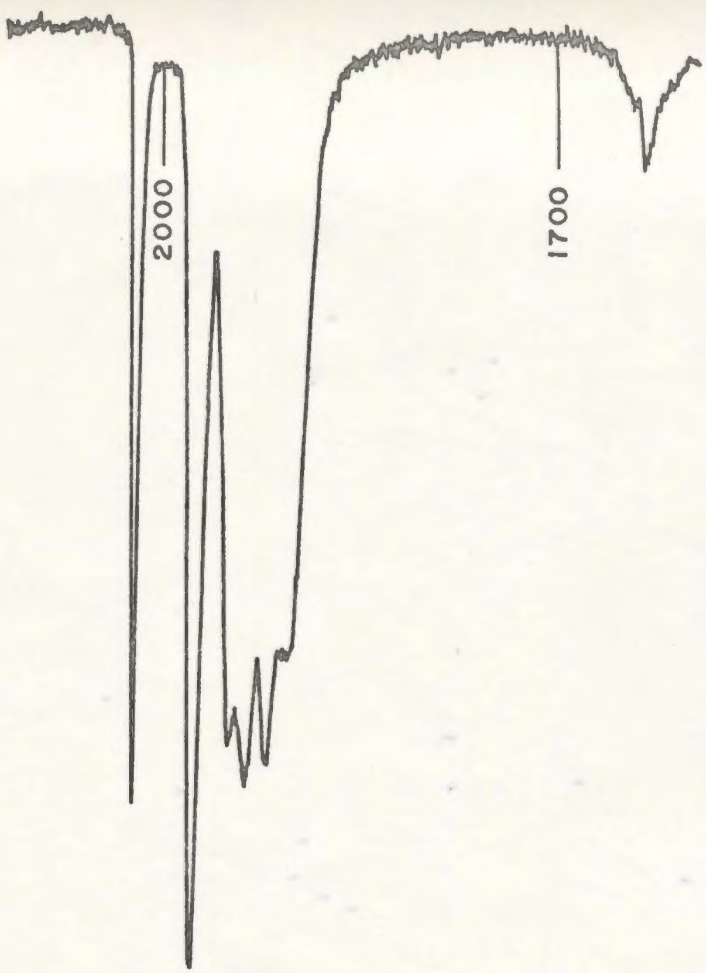
Substituents on the phenyl ring shift the C-O vibrations of $Cr(CO)_3$ complexed to the phenyl ring but do not seem to effect those of $Mn(CO)_3$. A decrease in the A_1 and E modes of the C-O stretching vibrations of $Cr(CO)_3$ is observed as shown in Table 3-4. The decreasing trend appears to be in the order H > m-CH_3 ≈ p-CH_3 ≈ o-CH_3 > p-OCH_3, and is illustrated in Fig. 3-3. This is in agreement with the M.O. treatment by Brown et al.[13,14], in which electron-donating substituents on the phenyl ring enhance 'back-donation' from the metal d-orbitals to the $p\pi^*$ orbitals of the carbonyls.

It is unfortunate that the halogen-substituted benzoyl ring does not complex with $Cr(CO)_3$ as readily as the halo-benzenes. It would be of interest to correlate substituent effects with the corresponding C-O stretching frequencies.



Spectrum 3-1

Infrared Spectrum of $C_6H_5COC_5H_4Mn(CO)_3$ (in CCl_4) (2100 - 1600 cm^{-1}).



Spectrum 3-2

Infrared Spectrum of $[(CO)_3Cr]C_6H_5COC_5H_4Mn(CO)_3$ (in CCl_4) (2100 - 1600 cm^{-1}).

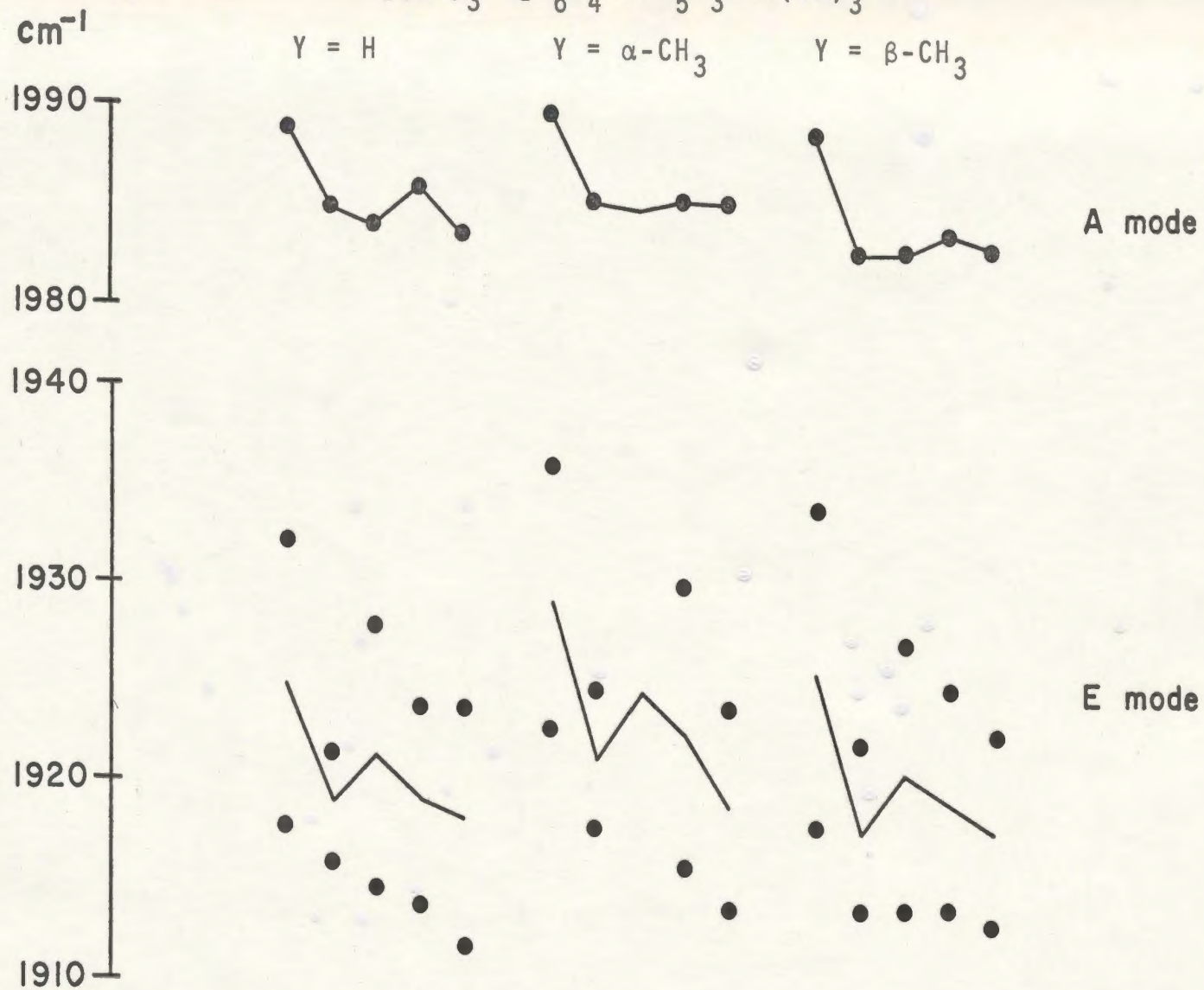
TABLE 3-4

Carbonyl Stretching Modes of Some $(CO)_3CrC_6H_4X\text{-}CO\text{-}C_5H_3YMn(CO)_3$ (cm^{-1})

		Y = H			Y = α-CH_3			Y = β-CH_3		
		A_1	E	ketonic ν(C-O)	A_1	E	ketonic ν(C-O)	A_1	E	ketonic ν(C-O)
X = H	$Mn(CO)_3$	2034	1960,1948	1643	2031	1954,1946	1644	2034	1958,1944	1641
	$Cr(CO)_3$	1989	1932,1918		1990	1936,1923		1989	1934,1918	
o-CH_3	$Mn(CO)_3$	2037	1962,1951	1652	2033	1958,1950	1660	2034	1958,1948	1652
	$Cr(CO)_3$	1985	1922,1916		1986	1952,1918		1983	1922,1914	
m-CH_3	$Mn(CO)_3$	2034	1960,1948	1645	-	-	-	2032	1957,1944	1643
	$Cr(CO)_3$	1984	1928,1915		-	-		1983	1927,1914	
p-CH_3	$Mn(CO)_3$	2033	1960,1949	1637	2034	1956,1949	1643	2032	1958,1945	1637
	$Cr(CO)_3$	1983	1924,1914		1986	1930,1916		1984	1925,1914	
p-OCH_3	$Mn(CO)_3$	2032	1960,1947	1639	2032	1957,1947	1643	2032	1957,1944	1639
	$Cr(CO)_3$	1984	1924,1912		1986	1924,1914		1983	1922,1913	

Effects of Substituents at Arene Ring on the CO vibrations of $Cr'CO)_3$ in

$[(CO)_3Cr]C_6H_4XCOC_5H_3YMn(CO)_3$



(The quintets are of the order X = H, X = o-CH_3, X = m-CH_3, X = p-CH_3 and X = p-OCH_3 respectively)

Fig. 3-3

The C-O stretching frequencies of the two $M(CO)_3$ moieties do not overlap (Spectrum 3-2). Hence, they are readily distinguishable. This is probably attributable to the fact that the chromium atom is more negatively charged than the manganese atom. As a result, the $d\pi$-$p\pi$ interactions between the chromium atom and the ligand are increased with a concomitant frequency decrease in the C-O stretching vibrations. The ring-metal bond order will be higher in the case of chromium than in manganese, a fact that will be borne out again in the discussion of mass spectroscopy (Chapter 7).

Comparison of the C-O stretching frequencies of $Cr(CO)_3$ in complexes $[(CO)_3Cr]C_6H_5CH_2C_5H_4Mn(CO)_3$ (1977 cm^{-1}, 1908 cm^{-1}) and $[(CO)_3Cr]C_6H_5COC_5H_4Mn(CO)_3$ (1989 cm^{-1}, 1925 cm^{-1}) shows that the $-COC_5H_4Mn(CO)_3$ entity is a stronger electron--withdrawing group than $-CH_2C_5H_4Mn(CO)_3$. Table 3-5 shows that if the C_5H_4- and C_6H_5-rings are not conjugated by a ketonic carbonyl group, no significant shifts to higher carbonyl stretching frequencies are observed. This shift to higher frequencies is not only a consequence of the electron withdrawing effect of the ketonic carbonyl as evident from the C-O stretching frequencies of $Cr(CO)_3$ in $[(CO)_3Cr]C_6H_5CH_2$-$COC_5H_4Mn(CO)_3$ (1976 cm^{-1}, 1908 cm^{-1}). Neither is this shift attributable to the conjugative effect alone since $[(CO)_3Cr]C_6H_5CH{=}CHC_5H_4Mn(CO)_3$ (1975 cm^{-1}, 1910 cm^{-1}) does not seem to show much deviation from $[(CO)_3Cr]C_6H_5CH_2C_5H_4Mn(CO)_3$. Perhaps this increased

TABLE 3-5

Carbonyl Stretching Modes of Some Miscellaneous Compounds of the Type R-$C_5H_4Mn(CO)_3$ (cm^{-1})

R	Uncomplexed		Complexed with $Cr(CO)_3$			
	C-O Modes of $Mn(CO)_3$		C-O Modes of $Mn(CO)_3$		C-O Modes of $Cr(CO)_3$	
	A_1	E	A_1	E	A_1	E
H-	2028	1945	-	-	-	-
CH_3-	2024	1942	-	-	-	-
C_6H_5-	2025	1941	2026	1947	1979	1913
$C_6H_5CH_2$-	2024	1938	2026	1945	1977	1908
$C_6H_5CH_2CO$-	2034	1958,1949	2034	1960,1950	1976	1909,1906
$C_6H_5CH_2CH(OH)$-	2026	1940	2026	1947,1938	1976	1907
$C_6H_5CH=CH$-	2022	1942	2024	1942	1975	1910

shift in C-O stretching frequency of $[(CO)_3Cr]C_6H_5COC_5H_4Mn(CO)_3$ is a consequence of both such effects.

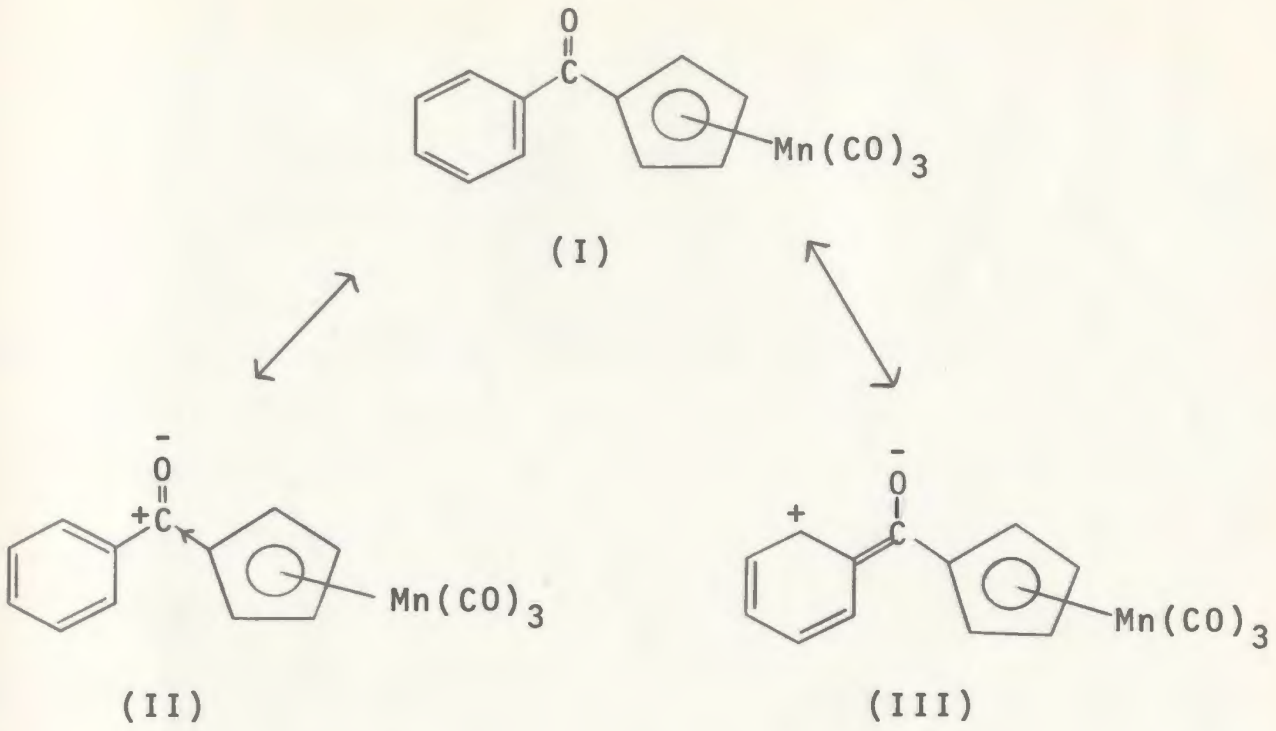
The loss of degeneracy of the E mode as indicated by the splitting of this mode into a doublet (Spectrum 3-1) is not altogether unexpected for such a large molecule. This supports Adams' view[11] that the C_{3v} local symmetry approximation for an $M(CO)_3$ group is inadequate if there are significant interactions between the ring and the C_{3v} site. This splitting is not very obvious in solution spectra of non-ketonic complexes (Table 3-5). It does appear that the ketonic carbonyl is mainly responsible for such a loss of C_{3v} symmetry. This may be due to the interactions of the $p\pi$-$p\pi$ orbital of the ketonic carbonyl and the ring which reduces the freedom of the ring-CO--ring rotation. Consequently, the $M(CO)_3$ moieties are more localised with respect to the whole molecule. This observation is further evidence that the $M(CO)_3$ moieties are not capable of free rotation about the metal-ring bond. Fig. 3-2 does appear to indicate that this splitting of the E modes is smallest when the methyl substituent on the cyclopentadienyl ring is next to the ketonic carbonyl group.

Ketonic Carbonyl Stretching Vibrations:

The stretching modes of the ketonic carbonyl group often reveal much information about the electronic effects

of the system. Though several workers[26] have discussed the vibrational modes of ketonic carbonyls it is not possible to associate such studies solely with electron distributions about the C-O bond. The frequency shifts of ν(CO) have been interpreted in terms of induction resonance, field effects, changes in the hybridisation with bond angle and on energy terms associated with stretching and bonding force constants of the CX and CY bonds in the ketones XCOY. It is not possible to measure the bond force constant of the ketonic carbonyl in such large molecules as described here because many factors which may contribute to this effect are involved. Only a comparative study of the ν(CO) frequencies will be attempted.

Table 3-3 shows that a methyl substituent on the cyclopentadienyl ring does not seem to affect the ketonic carbonyl frequency as much as if it was on the phenyl ring. When the substitution is at the ortho position of the phenyl ring a comparatively higher ν(C-O) frequency is observed whereas substitution of the methyl group at the α-position appears to show a slight decrease in ν(C-O) frequency. The $-C_5H_4Mn(CO)_3$ group may be considered to have a mainly inductive effect and the electronic effects may be visualised as in the figure below.



Structure II describes the $-C_5H_4Mn(CO)_3$ group as being co-ordinated to the ketonic carbon which is rendered slightly positively charged by the more electronegative oxygen adjacent to it. This co-ordination increases the electron density on the ketonic carbon thereby reducing the disparity of polarity of the C-O bond. This effect causes a decrease in the C-O bond order with concomitant decrease in ν(C-O) frequency.

The phenyl ring is best considered as conjugated to the ketonic CO (Structure III). It has a tendency to decrease the ν(C-O) frequency. The higher ν(C-O) frequencies observed for ortho substituted $CH_3C_6H_4COC_5H_4Mn(CO)_3$ is perhaps due to steric effects which subsequently tend to reduce the conjugation of the ring and the carbonyl group.

A significant decrease in ν(C-O) frequency is also observed for the para methoxy analogue. This decrease is probably due to the enhanced conjugation of the ring with the ketonic carbonyl group. It does appear that the substituents on the phenyl ring decrease the ν(C-O) frequencies in the order, o-Cl > o-F $\sim$ o-CH_3 > H $\sim$ m-F > p-Cl $\sim$ m-CH_3 $\sim$ p-CH_3 > p-OMe.

Bellamy and Pace[26] have compared the carbonyl basicity or proton accepting power of a series of saturated and unsaturated organic ketones with their corresponding carbonyl frequencies. They found that except for strained rings and conjugated systems, the carbonyl frequencies followed the same linear relationship with basicity. This relationship is a reasonable index of bond force constants. They suggested that for strained ring systems the increase in frequency is influenced primarily by coupling effects and there is little or no change in the carbonyl polarity. They further showed that for conjugated systems, the ν(C-O) frequencies could be altered without corresponding changes in the lone-pair electrons on the oxygen atom. Effectively, there is only a reduction of π-electron density on the carbonyl group while the hybridisation of the σ-bond remains unchanged. It is the latter which controls the polarity of the lone-pair electrons. It is not unreasonable, in view of the symmetry of the

orbitals involved, that there is not much interaction between the σ- and π-electrons of the C-O bond.

It is observed from Fig. 3-4 that the carbonyl frequencies are decreased when the arene ring of these ketones is complexed with a $Cr(CO)_3$ group. Proton NMR spectroscopy[27,28] shows that the π-character of the arene ring is not very much affected by the $Cr(CO)_3$ moiety, rather the σ-character is enhanced and the ring becomes more electronegative. If the inductive effect of the ring is considered alone then an increase in the carbonyl frequency is to be expected because the electronegative nature of the ring will tend to withdraw electrons from the carbon atom of the ketonic carbonyl, thereby increasing the polarity of the C-O bond. This effect is illustrated in Fig. 3-5a.

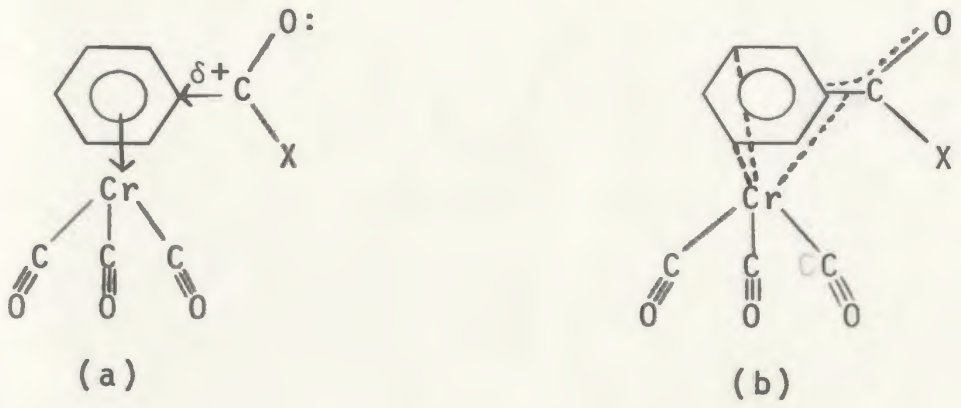
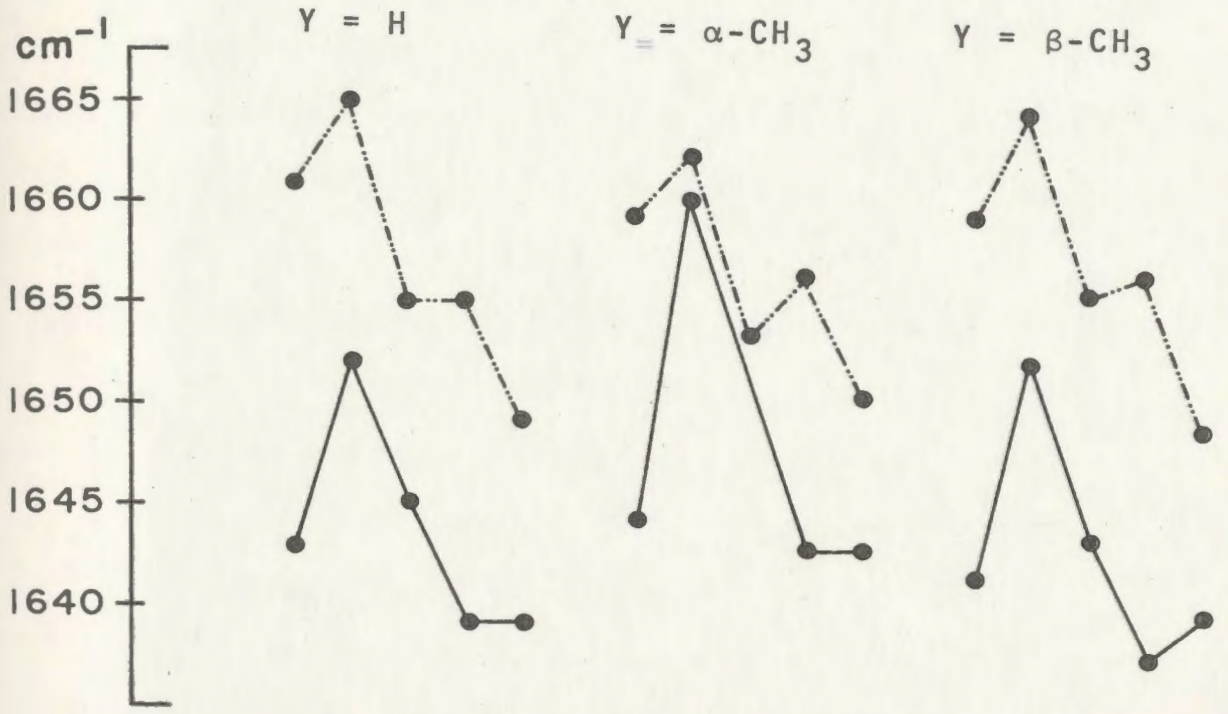


Fig. 3-5
Inductive-Conjugative Effects

It is therefore insufficient to consider the inductive effect alone as the π-effect is still predominant.

Fig. 3-4

Ketonic Carbonyl Frequencies of $C_6H_4XCOC_5H_3YMn(CO)_3$ Before (·····) and After (——) Complexing with $Cr(CO)_3$ Group



(The quintets are of the order X = H, X = o-CH_3, X = m-CH_3, X = p-CH_3 and X = p-OCH_3 respectively)

The ring-metal bond involves the interactions of the filled totally symmetric a_1 ring orbital with the 4s and $4p_z$ orbitals of the metal. The interaction is strengthened by the electron-withdrawing tendency of the three carbonyls. As a result the d-p separation of the ring-metal orbitals is decreased which allows a greater amount of mixing between the a_1 and b_2 orbitals of the ring and the appropriate metal orbitals. The preferred eclipsed configuration of arenechromium tricarbonyls of this type in which the Cr atom can be naively considered as having octahedral bonding[29], helps to explain this anomaly.

Fig. 3-5b shows that one of the bonds of chromium is directed towards the ketonic carbonyl group. This essentially withdraws π-electrons from the C-O bond. The main difference between this effect and inductive effect is that here the withdrawal is mainly that of π-electrons whereas in the latter case the withdrawal is mainly that of σ-electrons. As suggested by Bellamy and Pace[26] and more recently by Liler[30] these two effects are quite independent of each other. That this decrease in carbonyl frequency is indeed a conjugative effect is further evident from the high frequencies observed for ortho substituted methyl derivatives. For example, no significant decrease in carbonyl frequency was observed for α-CH_3, o-$CH_3C_6H_4COC_5H_3Mn(CO)_3$ (1662 cm^{-1}) and its corresponding $Cr(CO)_3$ complex (1660 cm^{-1}). This steric effect hinders the coplanarity of the π-system thereby reducing conjugation or alternatively the $Cr(CO)_3$

group no longer occupies the preferred configuration.

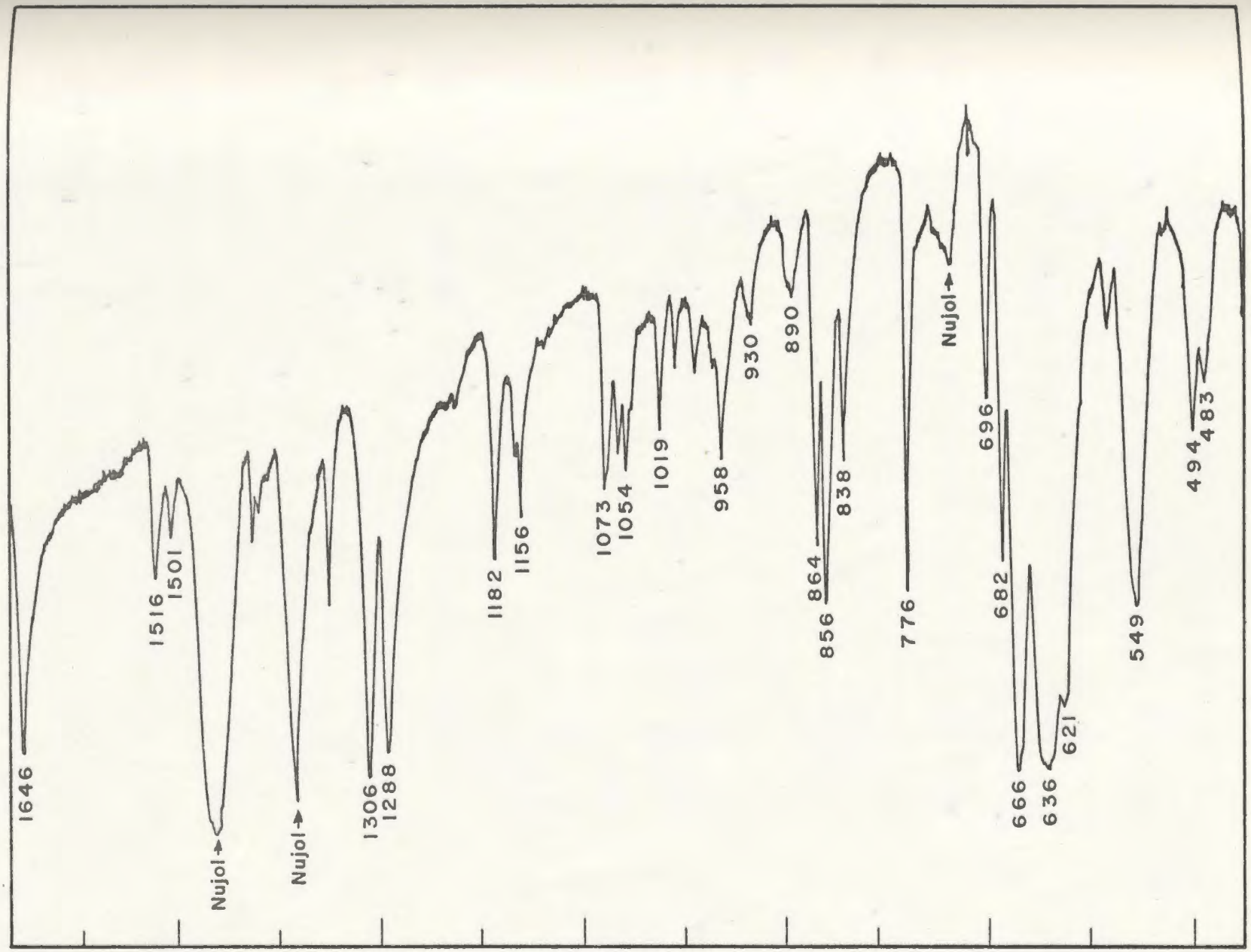
Nujol Mull Spectra:

The Nujol mull spectra of some derivatives of $C_5H_5Mn(CO)_3$ are presented in Table 3-6 and Table 3-7. The same decreasing trend in ketonic C-O stretching frequencies is observed for all the complexes upon variation of substituents. They are however, observed at lower frequencies than those of solution spectra. Furthermore, no significant change in this frequency is observed when these compounds are complexed with the $Cr(CO)_3$ moiety.

The ν(C-O) frequencies of the metal carbonyls are not measured because the bands are too broad and complicated to be of relevance. The following discussion is based on Spectrum 3-3 and Spectrum 3-4. The band at 1594 cm^{-1} of Spectrum 3-3 is assigned as the C=C stretch of the phenyl ring, but the weaker band at 1578 cm^{-1} may not be that of the cyclopentadienyl ring. It does appear to be of the same vibrational mode as the phenyl ring band at 1594 cm^{-1} because when the phenyl ring was complexed with $Cr(CO)_3$, both these bands were shifted to lower wavenumbers of 1516 cm^{-1} and 1501 cm^{-1} respectively (Spectrum 3-4). This shift can be readily explained as a weakening of the C-C bonds of the ring upon complexing with the $Cr(CO)_3$ moiety, which is capable of back-

Spectrum 3-3

Infrared Spectrum of $C_6H_5COC_5H_4Mn(CO)_3$ (Nujol Mull) (1650 - 480 cm^{-1}).



Spectrum 3-4

Infrared Spectrum of $[(CO)_3Cr]C_6H_5COC_5H_4Mn(CO)_3$ (Nujol Mull) (1650 - 480 cm^{-1}).

-donating to the pπ* orbitals of the ring. In other words, the aromaticity of the ring is reduced and in simple MO theory the filled ring orbital e_1 is capable of charge-transfer into the empty orbitals of the metal. This agrees with the observation by Humphrey[31] that complexing causes a shift to lower frequencies in the C=C stretch.

Most of the M-C-O bending, ring-M-$(CO)_3$ stretching and the M-C stretching modes are found in the region of 900 cm^{-1} and 300 cm^{-1}. The high intensity band at 741 cm^{-1} in Spectrum 3-3 is similar to that assigned to A_1 π(CH) mode in $C_6H_6Cr(CO)_3$[31] and $C_5H_5Mn(CO)_3$[5]. The possibility that this band is due to δ(MCO) is remote because only anionic carbonyls are known to have deformation modes so high[32]. Notice that Spectrum 3-4 shows the intensity of this band to be greatly reduced. In some cases this band was not observed at all when the arene ring of $XC_6H_4COMn(CO)_3$ was π-complexed with $Cr(CO)_3$ (Table 3-7). However, this band appears to have shifted from 745 cm^{-1} to about 780 cm^{-1} when X = OMe, F, or Cl.

The bands between 880 cm^{-1}, and 810 cm^{-1} observed in the spectrum of ferrocene[5] and cymantrene[6] have been assigned as CH (⊥) bending modes. The intense band observed at 868 cm^{-1} (Spectrum 3-3) is of the same order and tentatively assigned as A_1 and E_1 CH (⊥) bending modes.

It does appear that the band at 672 cm^{-1} in Spectrum 3-3 is the A_2 mode and the more intense band at 642 cm^{-1} the E mode. Lippincott[5] tentatively assigned the band at 541 cm^{-1} observed in $C_5H_5Mn(CO)_3$ to the A_1 Mn-CO bending mode. Perhaps, the band at 550 cm^{-1} is the A_1 Mn-CO bending mode. The medium to weak band at 504 cm^{-1} may be the Mn-C stretching mode and it is of interest to observe that this band is shifted to either 494 cm^{-1} or 483 cm^{-1} when the arene ring is complexed with the $Cr(CO)_3$ group. It is not possible to assign unambiguously whether this is the Mn-C stretching or the Cr-C stretching mode. In any case, this shift to lower frequency signifies that there is a net withdrawal of electron density from the cyclopentadienyl ring when the arene ring is π-complexed with $Cr(CO)_3$. This can be interpreted as a decrease in charge transfer from the cyclopentadienyl ring to the Mn atom resulting in a decrease of ring-Mn bond order but an increase in the C-O bond order, as previously observed.

EXPERIMENTAL

All the infrared spectra were recorded on a Perkin Elmer 457 grating spectrophotometer. Solution spectra were carried out using spectrograde carbon tetrachloride

(J.T. Baker, Chemical Co.) as solvent, and a 1 mm fixed pathlength cell with sodium chloride windows. Regions above 2,000 cm^{-1} were calibrated against the 2143.2 cm^{-1} band of CO, those between 2,000 and 1,800 cm^{-1} against DCl while regions below 1,880 cm^{-1} were calibrated against polystyrene. 2.5 scale-expansion was used in measuring regions above 1,600 cm^{-1}. All the spectra could be reproduced to within ± 1 cm^{-1}. Spectra of Nujol mulls were recorded using KBr cells. The intensities quoted in the tables are relative to the most intense band. The following notations are used, weak (w), medium(m), strong(s), very strong(vs), and shoulder (sh).

CONCLUSION

Generally, the CO stretching frequencies of the $M(CO)_3$ moieties are affected by substituents at the aromatic ring to which the $M(CO)_3$ moiety is complexed. Though the change is small, it nevertheless indicates that there is a significant overlap of the π-orbitals of the ring with those of the $M(CO)_3$ moiety.

The splitting of the E modes of the CO stretching frequencies shows that the $M(CO)_3$ moieties do not strictly have C_{3v} local symmetry. However, such an approximation is

adequate and is often useful in assigning absorption bands so long as one is aware of it.

The CO stretching frequency of the ketonic carbonyl is a good index of the electronic effects of substituents on the π- and σ-orbitals of the molecule.

TABLE 3-6

Infrared Spectra (Nujol Mull) in the Region 1700-400 cm^{-1}

Complex	
$C_6H_5COC_5H_4Mn(CO)_3$	1644(s), 1594(m), 1578(w), 1316(m), 1294(s), 1178(m), 1058(m), 1051(m), 1043(w), 1033(m), 980(m), 961(m), 953(w), 868(vs), 854(sh), 809(m), 741(s), 708(s), 684(sh), 672(s), 642(vs), 632(sh), 623(sh), 581(w), 550(s), 504(m), 446(w).
$C_6D_5COC_5H_4Mn(CO)_3$	1636(s), 1558(m), 1536(w), 1299(w), 1299(w), 1270(s), 1150(m), 1068(m), 1045(m), 1036(m), 964(m), 954(m), 939(w), 932(w), 876(m), 859(s), 846(s), 828(sh), 815(m), 806(w), 796(w), 738(m), 672(s), 666(sh), 644(vs), 634(sh), 614(sh), 554(m), 546(s), 496(w), 446(w).
$p\text{-}CH_3C_6H_4COC_5H_4Mn(CO)_3$	1688(w), 1634(s), 1600(s), 1564(w), 1314(m), 1289(s), 1174(s), 1126(w), 1116(w), 1064(w), 1058(w), 1041(m), 1022(w), 979(w), 961(w), 945(w), 932(w), 867(s), 852(s), 839(s), 796(m), 752(s), 674(s), 639(vs),

TABLE 3-6 (continued)

	631(sh), 618(sh), 556(s), 545(s), 500(w), 489(m), 441(w).
$p\text{-}OCH_3C_6H_4COC_5H_4Mn(CO)_3$	1634(vs), 1596(vs), 1506(s), 1326 (w), 1315(m), 1308(m), 1294(m), 1268(vs), 1226(sh), 1193(w), 1169 (vs), 1116(m), 1071(w), 1059(m), 1047(m), 1020(s), 970(w), 959(m), 938(w), 867(s), 844(vs), 795(m), 776(vs), 713(m), 670(s), 642(vs), 631(sh), 621(sh), 613(sh), 568(w), 544(vs), 522(m), 496(w), 444(w).
$p\text{-}ClC_6H_4COC_5H_4Mn(CO)_3$	1634(s), 1584(m), 1563(w), 1306(m), 1293(s), 1281(sh), 1185(w), 1173 (m), 1015(w), 1094(s), 1076(m), 1064(m), 1044(s), 1019(s), 976(w), 970(m), 956(m), 942(w), 911(sh), 863(vs), 851(vs), 772(vs), 752(vs), 732(s), 701(m), 671(s), 639(vs), 610(vs), 610(sh), 552(sh), 543(s), 496(s), 436(w).
$p\text{-}FC_6H_4COC_5H_4Mn(CO)_3$	1642(vs), 1599(vs), 1507(s), 1347 (s), 1309(s), 1296(s), 1276(sh), 1234(s), 1216(sh), 1188(m), 1161(s),

TABLE 3-6 (continued)

	1107(m), 1080(m), 1064(w), 1044(m), 1021(m), 974(m), 964(m), 943(w), 933(m), 874(s), 859(vs), 852(s), 816(s), 777(vs), 718(m), 677(s), 638(vs), 632(sh), 616(sh), 567(sh), 558(sh), 549(s), 518(s), 505(w), 438(m).
$o\text{-}ClC_6H_4COC_5H_4Mn(CO)_3$	1646(vs), 1586(m), 1303(s), 1281 (sh), 1270(sh), 1220(w), 1188(w), 1130(w), 1072(m), 1061(w), 1047(sh), 1040(s), 964(m), 956(m), 946(w), 928(m), 906(sh), 880(m), 865(sh), 861(s), 851(m), 840(sh), 784(m), 761(vs), 743(m), 715(s), 670(s), 656(m), 636(vs), 614(sh), 548(sh), 544(s), 496(m), 463(m), 450(w), 440(w).
$o\text{-}FC_6H_4COC_5H_4Mn(CO)_3$	1648(vs), 1608(s), 1576(w), 1480(m), 1306(s), 1265(m), 1225(s), 1186(m), 1156(w), 1107(m), 1071(w), 1057(m), 1044(m), 1036(w), 996(w), 965(m), 956(w), 930(w), 902(w), 878(s), 868 (vs), 860(s), 852(sh), 824(s), 786 (s), 774(vs), 720(m), 671(sh), 663(s),

TABLE 3-6 (continued)

636(vs), 624(sh), 620(sh), 551(sh),
543(s), 526(m), 496(m), 476(m),
464(w), 441(w), 413(w).

TABLE 3-7

Infrared Spectra (Nujol Mull) in the Range 1700-400 cm^{-1}

Complexes	
$[(CO)_3Cr]C_6H_5COC_5H_4Mn(CO)_3$	1646(vs), 1516(m), 1501(w), 1306(vs), 1288(vs), 1220(w), 1182(m), 1162(w), 1156(m), 1073(m), 1059(m), 1054(m), 1048(sh), 1019(m), 1004(w), 985(w), 958(m), 930(w), 890 (m), 864(s), 856(vs), 839(s), 776(vs), 696(s), 682(s), 666 (vs), 636(vs), 621(sh), 578 (vs), 494(s), 483(m), 443(w).
$[(CO)_3Cr]C_6D_5COC_5H_4Mn(CO)_3$	1614(vs), 1294(m), 1964(m), 1140(m), 1073(w), 1040(w), 964(w), 948(w), 930(w), 866 (w), 854(m), 844(m), 810(w), 790(w), 676(s), 673(s), 634 (vs), 618(sh), 615(sh), 590 (w), 571(w), 556(w), 541(sh), 534(s), 500(w), 486(m), 476 (w).

TABLE 3-7 (continued)

$[(CO)_3Cr]p\text{-}OCH_3C_6H_4COC_5H_4Mn(CO)_3$	1640(s), 1536(m), 1506(w), 1294(m), 1253(s), 1185(w), 1174(w), 1154(m), 1059(w), 1040(w), 1019(m), 958(w), 864(m), 837(m), 776(w), 686(m), 669(s), 644(s), 631(m), 616(sh), 567(w), 552(m), 526(w), 490(m), 438(w).
$[(CO)_3Cr]p\text{-}CH_3C_6H_4COC_5H_4Mn(CO)_3$	1634(s), 1536(w), 1296(m), 1284(m), 1169(w), 1155(w), 1042(w), 1016(w), 956(w), 946(w), 862(w), 856(w), 846(w), 793(w), 776(w), 676 (w), 666(sh), 660(m), 649 (m), 636(m), 624(m), 608 (sh), 564(w), 546(m), 536 (sh), 478(m).

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CHAPTER 4

ULTRA-VIOLET STUDIES

INTRODUCTION

Electronic spectroscopy has been widely used for determining the stereochemistry of many organometallic molecules as well as giving an insight into their electronic structures. Information pertaining to the nature of the metal-carbon bonds and the extent of electron delocalisation has also been deduced. For example, the electronic spectra of some Group V metal triphenyls show a single main peak near 250 nm which is not identifiable with either of the two readily observed benzene peaks. Jaffé[1] suggests that this is probably due to the interaction of the lone pair of electrons on the central metal atom with the ligands.

Two factors are responsible for impeding the assignment of electronic transitions in large molecules. The first factor deals with the broadness of the absorption bands which often envelope the less intense bands. These broad bands are due to the fact that in complex molecules, the multiplicity of vibrational sublevels and the closeness of their spacings cause the discrete bands to coalesce. The second factor involves the lack of symmetry in such complex molecules which subsequently leads to deviations from the selection rules based on symmetry and the orthogonality theorem. Transitions from a singlet

ground state to a triplet excited state which are normally forbidden in simple molecules have often been observed.

It is therefore not surprising that very little work has been carried out in this field. Spectral data on organometallic molecules are very limited and often very qualitative. Some attempts[2,3,4] have been made to correlate simple molecular orbital calculations with experimental data. Scott and Becker[5] assigned some of the observed bands of ferrocene but this has been reviewed by McGlynn[2] and Schachtschneider[3] who suggested that the two bands observed at 325 nm (E = 50) and 440 nm (E = 90) are those of e_{2g} ($3d_{xy}$, $3d_{x^2-y^2}$) $\longrightarrow$ e_{1g} ($3d_{xz}$, $3d_{yz}$) and a_{1g} ($3d_{z^2}$) $\longrightarrow$ e_{1g} transitions respectively. This has been supported by experimental data obtained by Barr and Watts[6]. Lundquist and Cais[7] studied a series of compounds of the types $RM(CO)_5$ and $M(CO)_6$. They consistently observed a band around 280 nm which they suggested is due to an electronic transition involving the metal-carbon bond. For convenience, these bands are to be referred as M-C bands. They also believe that the intense band around 210 nm is of similar nature. Ercoli and Mangini[8] observed three intense bands at 220 nm, 254 nm, and 320 nm in some arenechromium tricarbonyls which they believe were charge transfer bands from the chromium to the arene ring. They found that these bands were not significantly affected by variation of substituents on the arene ring.

RESULTS AND DISCUSSION

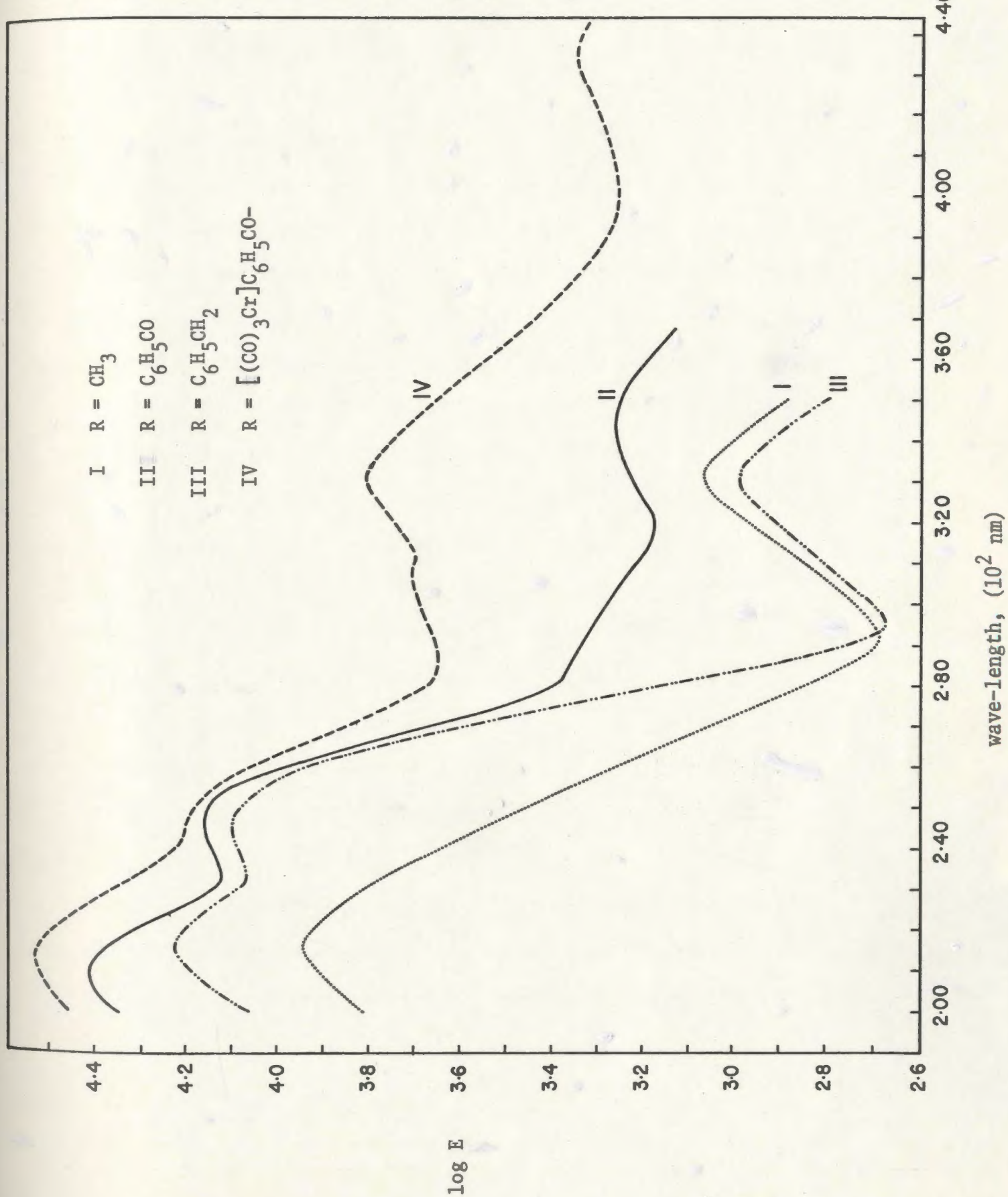
The lack of accurate experimental ultra-violet spectral data prevents the construction of accurate energy diagrams of organometallic complexes. Assignment of transitions of observed bands are often ambiguous and normally deduced from spectral studies of related compounds.

In the present work all the spectra were recorded in solutions and the results are summarised in Tables 4-1 and 4-2. The wave-lengths quoted carry an error of ± 2 nm while the E_{max} values can be read to an accuracy of ± 0.05 x 10^3.

Fig. 4-1 shows the spectra of several derivatives of cyclopentadienylmanganese tricarbonyl complexes. Spectra I and II have been studied by Lundquist and Cais[7]. They have assigned the bands between 325 nm and 350 nm to charge transfer Mn-C transitions. The bathochromic shift of this band from 331 nm (Spectrum I) to 344 nm (Spectrum II) is ascribed to the conjugative effect of the benzoyl group on the cyclopentadienyl ring. It is observed that the magnitude of the bathochromic shift increases with increase in conjugative effect of the substituents on the cyclopentadienyl ring. However, substituents on the arene ring do not seem to have significant effects on this band as evident from the spectra shown in Fig. 4-2. This confirms the results obtained

Fig. 4-1

Ultraviolet Spectra of some substituted cyclopentadienylmanganese tricarbonyl, $RC_5H_4Mn(CO)_3$



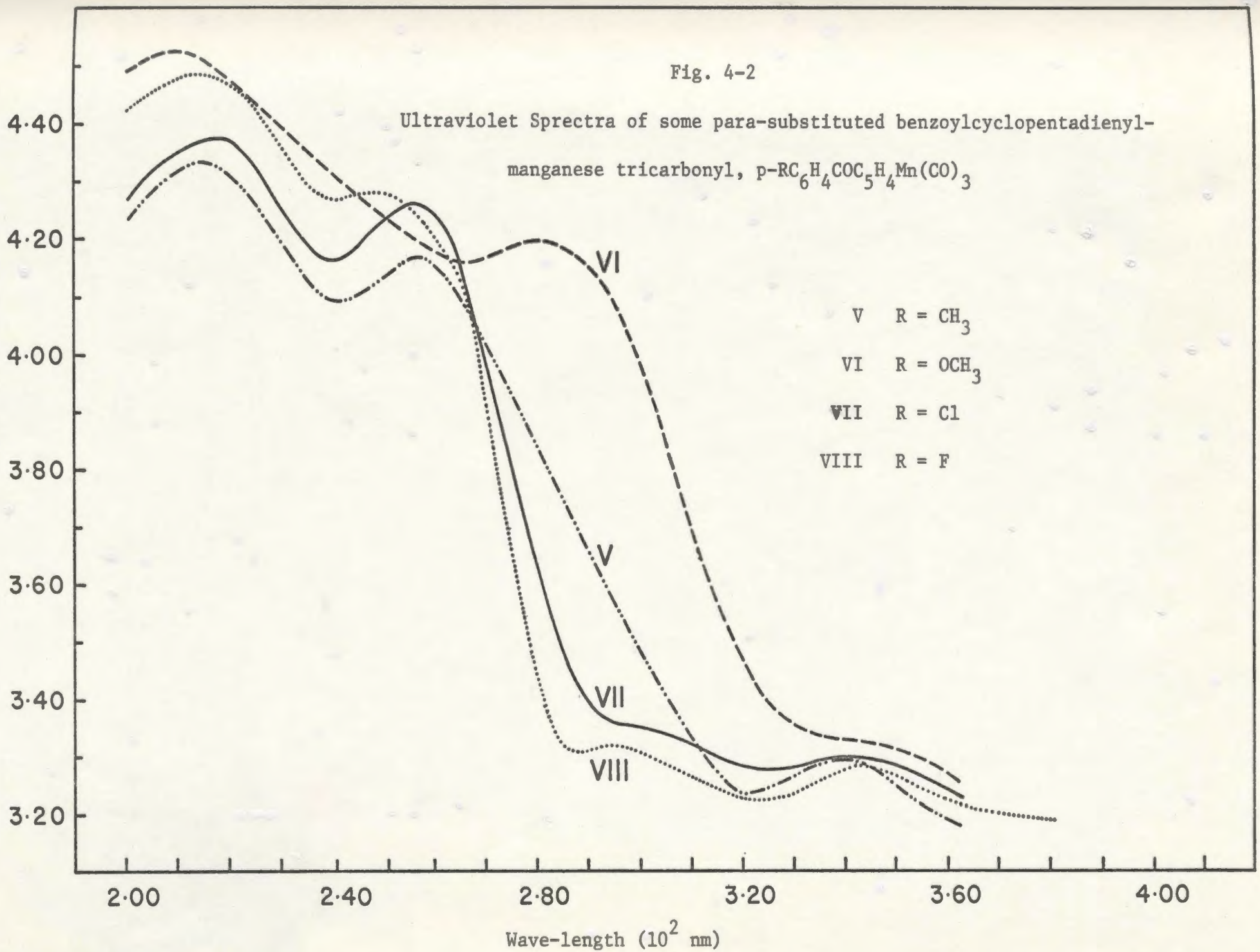
previously from infrared studies that substituents on the arene ring do not seem to have significant effects on the electronic environment of the CO's of the $Mn(CO)_3$ group.

A striking feature of the spectra in Fig. 4-2 is the sensitivity of the band around 250 nm to changes of substituents at the para position of the arene ring. This band shows a bathochromic shift which appears to be of the order p-OCH_3 > p-Cl ∿ p-CH_3 > p-F > p-H. The same order of bathochromic shift has been observed by Doub and Vanderbelt[9] in the $\pi \rightarrow \pi^*$ transition of the aromatic ring with changes in substituents. Moreover, Table 4-1 shows that generally the order of decreasing bathochromic shifts of this band is para > meta > ortho, which is in good agreement with increasing conjugative effect on the aromatic ring. It is therefore justifiable to assign tentatively the band at around 250 nm (Fig. 4-2) as the $\pi \rightarrow \pi^*$ transition of the arene ring. It is noteworthy that this transition is of comparable wave-length and intensity to those of acetophenone (240 nm, E = 13,000) and benzophenone (252 nm, E = 20,000)[10].

A comparatively weak shoulder is observed between 260 nm and 310 nm in all the spectra of the ketones presently studied. They are, however, very broad and often masked by the stronger band at shorter wave-lengths.

Fig. 4-2

Ultraviolet Sprectra of some para-substituted benzoylcyclopentadienyl-manganese tricarbonyl, p-$RC_6H_4COC_5H_4Mn(CO)_3$



g E

Hence it is difficult to correlate the shift of this band with substituent effects. Whether this is a $\pi \rightarrow \pi^*$ transition of the ketonic carbonyl[11] or another Mn-C band is difficult to ascertain.

The most intense band in the spectra of these complexes is around 210 nm. This band has been observed in the spectrum of cyclopentadiene as well as in those of metal-carbonyls such as $M(CO)_6$. Though Lundquist and Cais[7] have assigned this to a M-C band, it is equally likely that this is attributed to the cyclopentadienyl ring. The fact that this band appears at the lower limits of the spectral scan where the sensitivity of the instrument is greatly reduced, makes deduction from it meaningless.

π-Complexing of the $Cr(CO)_3$ group onto the arene ring reduces the π-electron density on the aromatic ring system. This reduction brings about a loss of conjugative effect in the system and a subsequent hypsochromic shift of the Mn-C band is expected. Indeed Spectrum IV in Fig. 4-1 shows that the Mn-C band has been shifted to lower wave-length, (330 nm). At the same time the intensity of this band is also observed to have increased relative to Spectrum II. A decrease in conjugation is generally followed by a decrease in intensity[12]. The fact that the reverse order is observed here suggests that perhaps this shift is not just a conjugative effect and that the polarity of the substituent must also be

considered.

A weak band at 434 nm ($E = 2.2 \times 10^3$) is also observed in Spectrum IV. In fact this band has only been observed when a $Cr(CO)_3$ group is co-ordinated to the arene ring (Table 4-2). Surprisingly, this band has not been reported by Ercoli and Mangini[8], or Lundquist and Cais[7], in their studies of arenechromium tricarbonyl complexes. This band is not very sensitive to substituent changes on the arene ring, except perhaps with $[(CO)_3Cr]o\text{-}CH_3C_6H_4COC_5H_4Mn(CO)_3$ and $[(CO)_3Cr]C_6H_4\text{-}CH{=}CHC_5H_4Mn(CO)_3$ where hypsochromic shifts are observed. A subsequent reduction in intensities of these bands is also observed. It is very likely that these observations are due to a loss of conjugation in the whole system. A similar but much less intense band has been reported for ferrocenyl complexes in which a d-d transition of the type $a_{1g}\ (3d_z2) \longrightarrow e_{1g}$, has been tentatively assigned. Gray and Beach[13] observed a band at 440 nm in the spectrum of $Cr(CO)_6$ which they proposed to be of the same nature as that observed in ferrocene; a charge transfer band from metal to ligand. It is therefore reasonable to assign the band observed at 434 nm in Spectrum IV to a charge transfer Cr-C band.

TABLE 4-1

Ultra-violet Spectral Data of X-$C_5H_3(Y)Mn(CO)_3$

X	Y=H		Y=α-CH_3		Y=β-CH_3	
	(nm)	$E_{max}(10^3)$	(nm)	$E_{max}(10^3)$	(nm)	$E_{max}(10^3)$
H-	331	0.86	331	1.15	-	-
	216	11.6	216	8.82	-	-
C_6H_5CO-	344	1.75	347	1.01	345	2.03
	282	2.34	276	1.25	286(sh)	2.26
	247	14.6	245	8.57	247	13.9
	209	25.9	215	12.9	215	20.4
o-$CH_3C_6H_4CO$-	337	1.62	341	1.76	-	-
	285	4.68	280	2.68	-	-
	243	9.80	247(sh)	10.6	-	-
	211	23.5	213	26.4	-	-
m-$CH_3C_6H_4CO$-	339	1.58	343	2.02	410	0.46
	289	4.50	284	3.66	322	2.17
	251	11.7	248	17.9	253	5.42
	215	17.3	218	27.8	212	17.5
p-$CH_3C_6H_4CO$-	339	1.97	338	2.73	338	1.99
	257	14.9	257	22.6	257	8.74
	215	22.1	213	33.9	213	13.9

TABLE 4-1 (continued)

X	Y=H		Y=α-CH_3		Y=β-CH_3	
	(nm)	$E_{max}(10^3)$	(nm)	$E_{max}(10^3)$	(nm)	$E_{max}(10^3)$
o-FC_6H_4CO-	342	2.00	-	-	-	-
	278	2.87	-	-	-	-
	239	15.8	-	-	-	-
	216	21.9	-	-	-	-
m-FC_6H_4CO-	347	2.14	350	2.01	-	-
	285	3.31	280	3.32	-	-
	243	17.0	240	19.2	-	-
	218	20.1	216	25.5	-	-
p-FC_6H_4CO-	343	1.93	342	2.40	-	-
	294	2.12	299	2.21	-	-
	249	1.91	249	17.1	-	-
	213	31.8	217	21.2	-	-
o-ClC_6H_4CO-	341	1.95	345	2.02	342	1.96
	285	2.51	286	2.31	287	2.22
	238	14.5	243	17.0	244	12.1
	216	30.4	216	36.3	219	19.4
p-ClC_6H_4CO-	342	21.6	348	2.11	344	2.30
	298	2.23	290	2.02	300	3.41
	257	18.1	257	20.1	256	20.0
	217	24.5	217	26.6	218	23.2

TABLE 4-1 (continued)

X	Y=H		Y=α-CH_3		Y=β-CH_3	
	(nm)	$E_{max}(10^3)$	(nm)	$E_{max}(10^3)$	(nm)	$E_{max}(10^3)$
p-$OCH_3C_6H_4CO$-	340	2.13	339	2.26	336	2.40
	280	15.7	280	16.6	281	17.1
	209	34.2	212	32.4	225	26.4
	-	-	-	-	213	34.5
$C_6H_5CH_2$-	331	0.97	330	1.04	331	1.14
	246	12.6	223	15.6	220	16.3
	216	16.8	-	-	-	-
C_6H_5CH=CH-	284	9.51	-	-	-	-
	212	16.1	-	-	-	-
$C_6H_5CH_2CO$-	336	1.41	-	-	-	-
	280	2.11	-	-	-	-
	236	7.05	-	-	-	-
	218	12.8	-	-	-	-

TABLE 4-2

Ultra-violet Spectral Data of X-$C_5H_3(Y)Mn(CO)_3$

X	Y=H		Y=α-CH_3		Y=β-CH_3	
	(nm)	$E_{max}(10^3)$	(nm)	$E_{max}(10^3)$	(nm)	$E_{max}(10^3)$
$[(CO)_3Cr]C_6H_5CO-$	434	2.20	433	2.22	433	2.56
	330	6.32	329	6.27	330	7.27
	307	4.98	251	9.64	244	9.43
	244	16.14	213	28.9	213	31.6
	214	34.70	-	-	-	-
$[(CO)_3Cr]o\text{-}CH_3C_6H_4$	420	8.33	427	1.96	426	1.61
	309	3.95	316	6.70	316	6.15
	245	9.90	254	19.2	248	11.9
	209	31.0	215	58.0	209	33.4
$[(CO)_3Cr]m\text{-}CH_3C_6H_4CO-$	435	2.66	-	-	435	2.64
	331	6.87	-	-	332	6.79
	246	11.22	-	-	300	5.38
	210	32.41	-	-	249	14.2
$[(CO)_3Cr]p\text{-}CH_3C_6H_4CO-$	435	3.05	433	3.45	211	37.3
	331	8.60	330	9.80	433	3.54
	252	16.24	253	18.16	331	10.31
	212	50.72	213	52.34	266	7.87

TABLE 4-2 (continued)

X	Y=H		Y=α-CH_3		Y=β-CH_3	
	(nm)	$E_{max}(10^3)$	(nm)	$E_{max}(10^3)$	(nm)	$E_{max}(10^3)$
$[(CO)_3Cr]p\text{-}OCH_3C_6H_4CO\text{-}$	437	1.54	437	2.44	249	23.25
	335	3.85	336	7.43	210	62.14
	291	3.32	287	6.3	437	3.15
	236	15.44	236	24.3	337	9.34
	216	18.46	218	39.4	292	7.86
$[(CO)_3Cr]C_6H_5CH{=}CH\text{-}$	415	0.51	-	-	237	34.3
	328	1.43	-	-	216	55.3
	262	2.64	-	-	-	-
	213	5.63	-	-	-	-

EXPERIMENTAL

All the ultra-violet spectra were recorded on a SP 800 UV spectrophotometer, using 1 cm quartz cells. Solutions of approximately 5 x 10^{-4}M were prepared using spectrograde hexane (Fisher Scientific Co.) as solvent. Appropriate dilutions were made to obtain transmittance in the range of 2 to 80%. All the bands were calibrated with bands of holmium oxide.

The logarithmic molar extinction coefficients were plotted against wave-lengths at intervals of 20 nm. Intervals of 5 nm were used at points of inflexions.

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CHAPTER 5
NUCLEAR MAGNETIC RESONANCE STUDIES

INTRODUCTION

Assignment of Proton Resonance Frequencies.

NMR spectroscopy has been extensively used to study the electronic effects of π-complexes such as ferrocene[1,2] and bis-π-benzenechromium[3,4]. Such studies are often made difficult by the lack of definitive assignment of proton resonance frequencies. The resonances of the α- and β-protons of mono-substituted cyclopentadienyl complexes have been assigned by analogy to the effects of substituents on the chemical shifts of mono-substituted benzene protons. For example, Moreland et al.[6] observed that the chemical shift difference between the ortho and meta protons of benzoyl derivatives is very similar to the difference observed for the α- and β-protons of carbonyl substituted cyclopentadienylmanganese tricarbonyls. Both the α- and β-protons are shifted downfield; the lower field resonances being those of the α-protons. Rausch and Siegel[7] selectively deuterated a series of ferrocene derivatives and concluded unambiguously that electron-withdrawing substituents always shift α-proton resonances to lower fields than those of the β-protons. Such selective deuterations are at times either not

feasible or are often very tedious. Kamezawa[8] found that a trend exists between coupling constants of protons meta to one another. The meta coupling between two protons adjacent to the substituent is larger than the other, i.e. $J_{25} > J_{34}$. A similar trend has been observed by Mayo and Goldstein[9] for mono-substituted benzene derivatives. The meta coupling between two protons adjacent to the substituent, J_{26}, increases with increasing electronegativity of the substituent while the J_{24} coupling decreases.

Substituent Effects.

It does appear that the analysis of NMR spectra of mono-substituted cyclopentadienyl complexes is less complicated than mono-substituted benzenes since the former contain only two distinct homoannular positions. However, electronic perturbation of a five-membered aromatic ring is more difficult to interpret and the relative shielding and deshielding of the ring protons depends mainly on the electronic character of the substituent.

Slocum and Ernst[10] found that the substituents in mono-substituted ferrocenes may be classified into four categories according to their relative shielding and deshielding effects on the ring protons.

1) Substituents which deshield both α- and β-protons.

2) Substituents which shield both α- and β-protons.

3) Substituents which shield the α-protons and deshield the β-protons.

4) Substituents which deshield the α-protons and shield the β-protons.

They concluded that resonance effects of the substituents are mainly felt by the β-protons whereas inductive effects are reflected by the α-protons. This conclusion, however, is open to doubt since it has been found that the α-protons are more sensitive than the β-protons to conjugative effects[11]. Furthermore, Moreland et al.[6] observed that the α- and β-protons are affected by substituents to the same extent as the ortho and meta protons of mono-substituted benzene.

The NMR studies of arenechromium tricarbonyl complexes have drawn considerable interest. This is mainly due to the fact that the chemical reactivity of these complexes does not seem to agree with the spectral results. Most of the reaction studies indicate that the $Cr(CO)_3$ group withdraws π-electrons from the arene ring[12,13] whereas NMR studies show that the π-effect of the aromatic ring is not different from that of the free aromatic ring. McFarlane and Grim[14], Gubin and Khandkarova[15,16], and Reeves et al.[17] proposed that the $Cr(CO)_3$ group affects mainly the σ-carbon orbitals of the ring. More recently, Bodner and Todd[18] carried out some ^{13}C NMR studies of arenechromium tricarbonyl complexes and they interpreted their results in terms of a net withdrawal

of electron density by the $Cr(CO)_3$ group from the σ-framework of the arene ring.

Upfield Shift of Arene Proton Resonance of π-$Cr(CO)_3$ Complexes.

An interesting feature in the spectra of these complexes is that when the arene ring is complexed with a $Cr(CO)_3$ group, the ring proton resonances are shifted up-field by about 2 ppm[19,20,21]. Many explanations have been proposed and are summarised below.

i) The π-electron withdrawing effect of the $Cr(CO)_3$ group is capable of reducing the electron density on the arene ring. As a result, the ring current of the π-electrons which is responsible for the lower chemical shift of aromatic ring protons relative to the normal alkene protons is reduced[22]. This explanation, however, is not able to account for the same upfield shift observed in π-$Cr(CO)_3$ complexes of olefins[23] where no ring currents are present.

ii) The $Cr(CO)_3$ group has three-fold symmetry, hence its magnetic anisotropy will also have three-fold symmetry. Emanual and Randall[24] believe that this effect can bring about an upfield shift in the arene proton resonances.

iii) The average shielding factor in Ramsey's formula is a sum of the diamagnetic and paramagnetic terms, i.e. $\sigma_{av.} = \sigma_d + \sigma_p$. Gubin et al.[16] believe that this upfield

shift may be due to a change in the paramagnetic contribution upon complexing with a $Cr(CO)_3$ group.

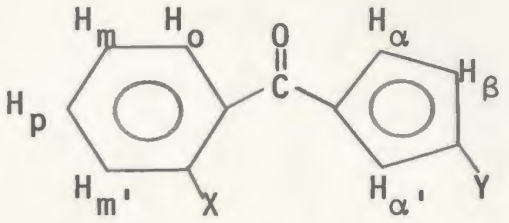
Solvent Effects

The chemical shifts of protons in arenechromium tricarbonyl complexes differ from solvent to solvent. The proton resonance of $C_6H_6Cr(CO)_3$, for example, was found to be shifted upfield by about 0.8 ppm when benzene[19] was used as solvent instead of chloroform[14]. A low field shift was observed when acetone was used[26]. This has been attributed to the proton-acceptor property[27] of the solvent which tends to shift the electrons from the proton to the solvent. As a result, the electron density and the magnetic screening of the proton associated with it are reduced. Mangini and Taddei[26] found that generally, the more acidic the proton the stronger is the shift, hence the arene protons of π-$Cr(CO)_3$ complexes are affected more than those of the free arene ring.

In order to obtain accurately comparable chemical shifts of these anisotropic complexes, it is necessary to carry out the measurements in solutions of [redacted] isotropic solvents such as cyclohexane or carbon tetrachloride. Unfortunately, most of these complexes are only sparingly soluble in these solvents and it is found that deuterochloroform gives comparatively good results.

RESULTS AND DISCUSSION

The following positional nomenclature is employed.



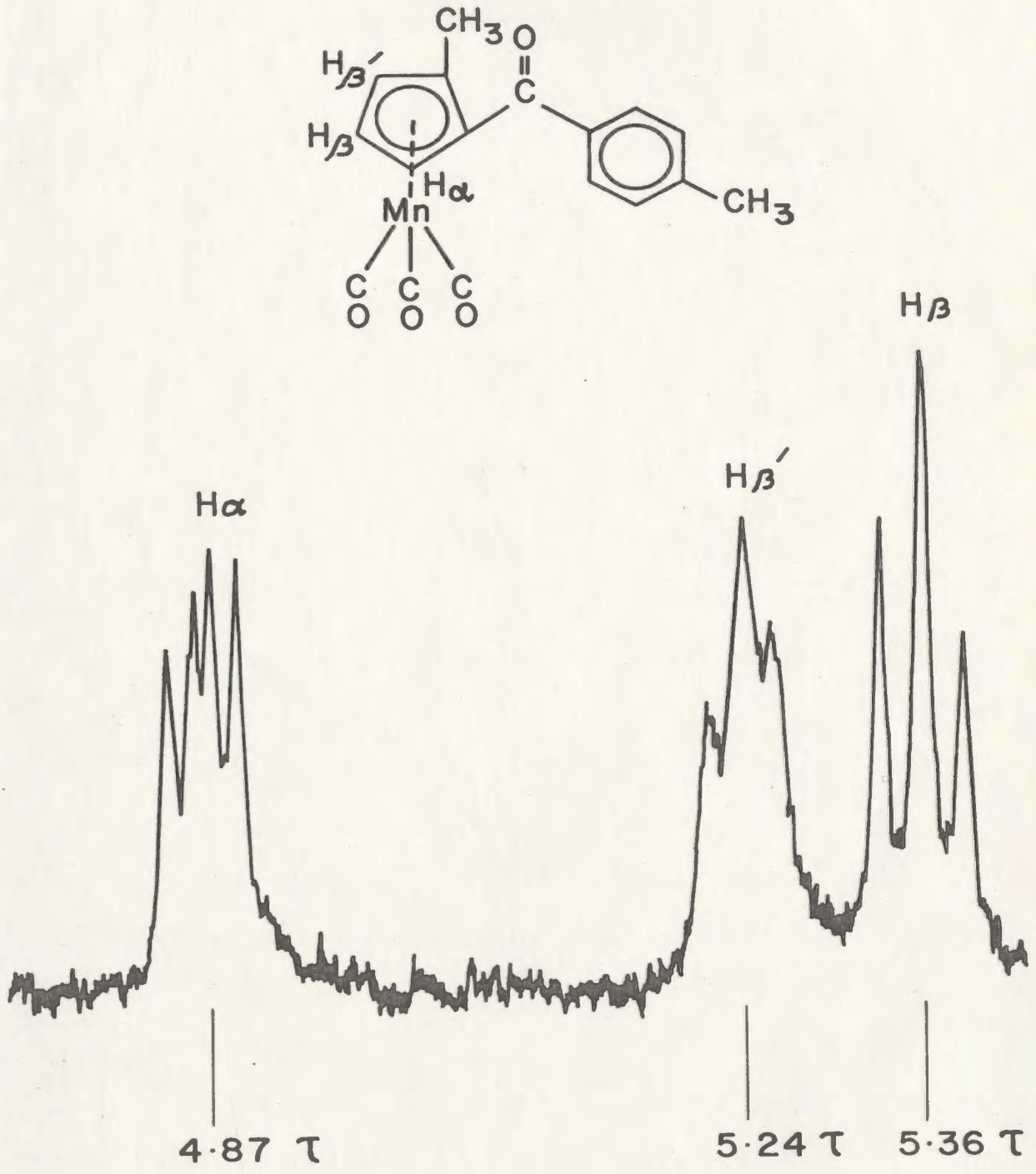
Whenever two protons are situated at equivalent positions with respect to the ketonic carbonyl group, a subscript is used for the proton nearer the substituent.

Cyclopentadienyl Proton Resonances.

The α- and β-proton resonances of the mono-substituted cyclopentadienyl ring are readily assigned since the former are nearer to the electron-withdrawing carbonyl group and are therefore expected at lower fields. In cases where there is another substituent on the cyclopentadienyl ring, the corresponding α, α' and β, β' proton resonances are more difficult to assign. It is observed that a methyl group at the α-position normally results in three separate resonances attributed to the three protons of the cyclopentadienyl ring. The spectrum of α-methyl, p-toluylcyclopentadienylmanganese tricarbonyl [p-$CH_3C_6H_4$-COC_5H_3(α-CH_3)$Mn(CO)_3$] (Spectrum 5-1) shows only the region where the cyclopentadienyl proton resonances appear.

Spectrum 5-1

NMR spectrum of p-$CH_3C_6H_4COC_5H_3(\alpha\text{-}CH_3)Mn(CO)_3$ in $CDCl_3$ showing the cyclopentadienyl proton resonances

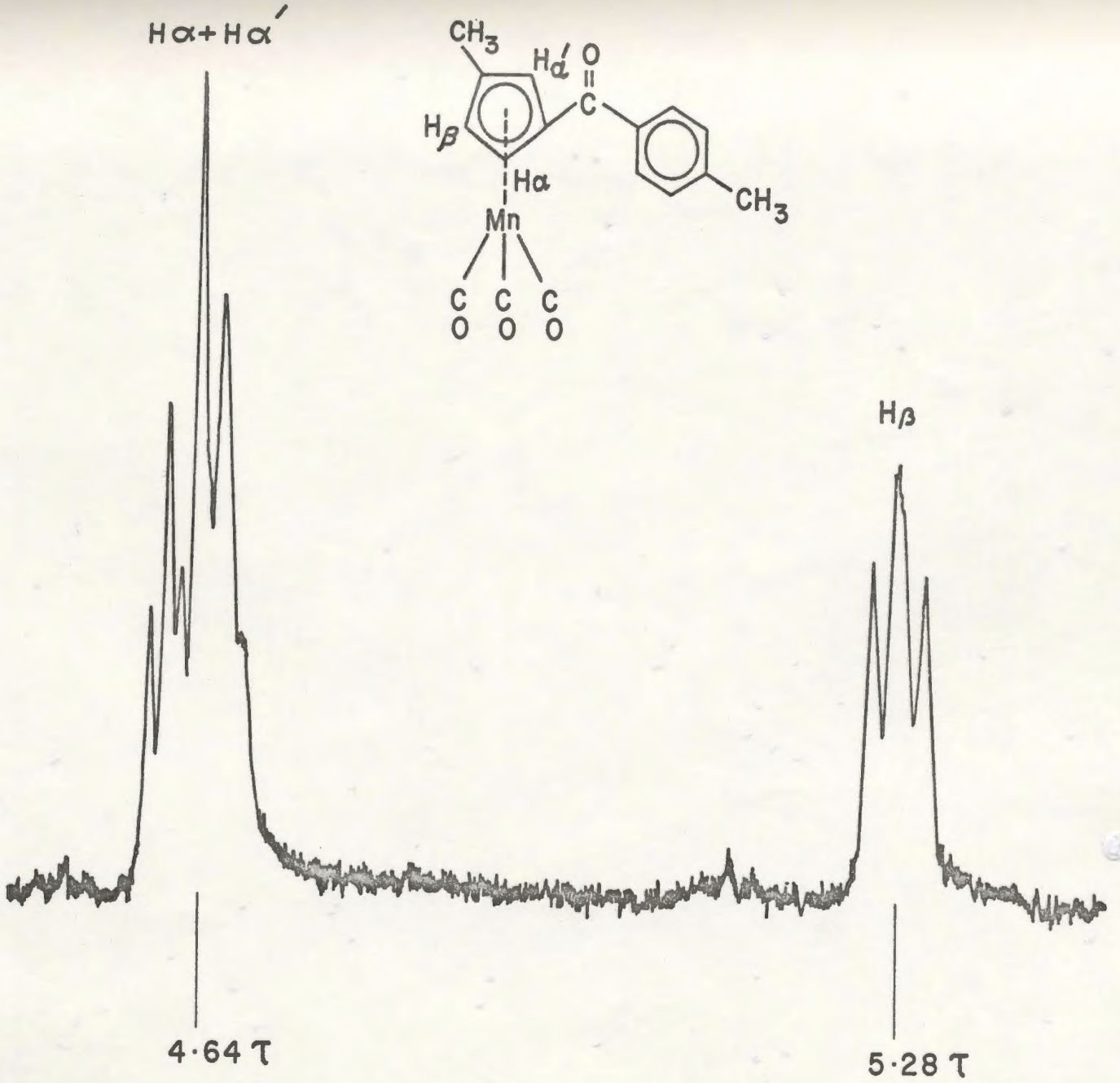


The doublet of doublets at 4.87 τ is assigned to the α-protons ($J_{\alpha\beta}$ = 2.7 cps, $J_{\alpha\beta}'$ = 1.8 cps), while the triplet at 5.36 τ is tentatively assigned to the β-proton ($J_{\alpha\beta}$ = $J_{\beta\beta}'$ = 2:7 cps). The multiplet at 5.24 τ is not well resolved and is assigned to the β'-proton; the small coupling constants may be due to the adjacent methyl protons. This assignment is consistent with that of Moreland et al.[6].

When the methyl group is substituted at the β-position of the cyclopentadienyl ring, the α and α' proton resonances appear to coincide making it more difficult to assign them accurately. The β-proton resonance is observed at 5.28 τ. This is shown in the spectrum of β-methyl, p-toluylcyclopentadienylmanganese tricarbonyl (Spectrum 5-2).

Substituent Effects on Cyclopentadienyl Proton Resonances.

Generally, the cyclopentadienyl proton resonances occur at lower fields than those observed for $C_5H_5Mn(CO)_3$ (5.28 τ) (Table 5-1). This is mainly due to the withdrawal of π-electron density from the ring by the carbonyl substituent. The deshielding effect appears to be more pronounced at the α-positions of the cyclopentadienyl ring. The chemical shift observed for $C_5H_5Mn(CO)_3$ protons (5.28 τ) in $CDCl_3$ is very much higher than the value 5.04 τ



Spectrum 5-2

NMR Spectrum of p-$CH_3C_6H_4COC_5H_3(\beta\text{-}CH_3)Mn(CO)_3$ in $CDCl_3$ showing the cyclopentadienyl proton resonances

observed by Moreland et al.[6] in DMSO. This difference is probably due to the strong proton-accepting property of DMSO.

The cyclopentadienyl protons are apparently not affected by substituents at the meta and para position of the phenyl ring. Ortho substituents tend to shift the α-proton resonance of the cyclopentadienyl ring slightly upfield, but leave the β-protons unaffected. This is perhaps due to the ortho substituents sterically hindering coplanarity of the π and π* orbitals of the ketonic carbonyl with the π orbitals of the arene ring. This is further supported by the methyl substituent at the α-position of the cyclopentadienyl ring inducing a further shift to higher fields of the α-protons. If the shift is assumed to be additive, then it appears that the methyl substituent at the α-position of the cyclopentadienyl ring is more effective as a steric group than the methyl at the ortho position of the arene ring (column 2 and 4, Table 5-1). It is noteworthy that the resonances of the α-methyl protons are at lower fields than those of the β-methyl protons. The fact that a sharp singlet has been observed for this resonance shows that there is no significant interaction between the α-methyl protons and the ketonic carbonyl group. Perhaps this low field shift is a result of the hyperconjugative

TABLE 5-1

NMR Spectral Data of Cyclopentadienyl Protons of Some

$X\text{-}C_6H_4COC_5H_3(Y)Mn(CO)_3$ Complexes ($\tau \pm 0.001$ ppm)

X	Y = H		Y = α-CH_3				Y = β-CH_3			
	H_α	H_β	H_α	H_β	$H_{\beta'}$	H(Y)	H_α	$H_{\alpha'}$	H_β	H(Y)
H	4.51	5.11	4.89	5.37	5.23	7.70	4.63	4.63	5.22	7.90
o-CH_3	4.61	5.13	5.02	5.41	5.23	7.73	4.75	4.75	5.29	7.97
o-Cl	4.67	5.14	5.02	5.39	5.21	7.76	4.75	4.79	5.27	7.98
o-F	4.59	5.14	-	-	-	-	-	-	-	-
o-OH	-	-	-	-	-	-	4.57	4.57	4.62	-
m-CH_3	4.54	5.14	4.87	5.33	5.23	7.72	4.63	4.63	5.27	7.94
m-F	4.54	5.11	4.90	5.34	5.21	7.70	-	-	-	-
p-CH_3	4.54	5.15	4.87	5.36	5.24	7.73	4.62	4.66	5.28	7.98
p-Cl	4.54	5.10	4.92	5.35	5.21	7.71	4.67	4.67	5.26	7.95
p-F	4.53	5.11	-	-	-	-	4.66	4.66	5.25	7.95
p-OCH_3	4.53	5.13	4.89	5.36	5.26	7.74	4.65	4.65	5.28	7.95

effect of the methyl group being reduced by the π-effect of the ketonic carbonyl group.

Cyclopentadienyl Proton Resonances of π-$Cr(CO)_3$ Complexes.

The spectral results are as tabulated in Table 5-2 and Table 5-3. The value ΔH in Table 5-3 is defined by the equation

ΔH (ppm) = H (before complexing) - H (after complexing).

It is observed that when the arene ring is complexed with a $Cr(CO)_3$ group, a shift to lower field is observed for the cyclopentadienyl protons.

This downfield shift is probably due to the withdrawal of π-electrons from the $-C_5H_4Mn(CO)_3$ moiety by the $Cr(CO)_3$ group. Such an effect is expected to shift the resonance of the α-methyl protons of the cyclopentadienyl ring downfield. The fact that an upfield shift is observed suggests that perhaps this is due to anisotropic field effects of the $Cr(CO)_3$ group

Arene Proton Resonances

The various arene proton resonances are often difficult to assign without labelling studies. In the systems considered here, they have either been observed as well resolved signals or as multiplets.

TABLE 5-2

NMR Spectral Data of Cyclopentadienyl Protons of Some

$[(CO)_3Cr]XC_6H_4COC_5H_3YMn(CO)_3$ Complexes ($\tau \pm 0.001$ ppm)

X	Y = H		Y = α-CH_3				Y = β-CH_3			
	H_α	H_β	H_α	H_β	$H_{\beta'}$	H(Y)	H_α	$H_{\alpha'}$	H_β	H(Y)
H	4.40	5.09	4.82	5.30	5.22	7.78	4.52	4.61	5.23	7.94
o-CH_3	4.42(4.55)*	5.09	4.97	5.35	5.17	7.75	4.71	4.60	5.23	7.95
m-CH_3	4.46	5.09	-	-	-	-	4.63	4.54	5.25	7.94
p-CH_3	4.50	5.11	4.72	5.35	5.24	7.80	4.52	4.62	5.25	7.93
p-OCH_3	4.45	5.11	4.70	5.31	5.25	7.81	4.53	4.62	5.26	7.95

*(Possible formation of rotational isomers)

TABLE 5-3

Perturbation of the Cyclopentadienyl Proton Resonances by the $Cr(CO)_3$ Moiety of Some $[(CO)_3Cr]XC_6H_4COC_5H_3YMn(CO)_3$ Complexes

X	Y = H		Y = α-CH_3				Y = β-CH_3			
	ΔH_α	ΔH_β	ΔH_α	ΔH_β	$\Delta H_{\beta'}$	$\Delta H(Y)$	ΔH_α	$\Delta H_{\alpha'}$	ΔH_β	$\Delta H(Y)$
H	0.11	0.02	0.07	0.07	0.01	-0.08	0.11	0.02	-0.01	-0.04
o-CH_3	0.19(0.06)	0.04	0.05	0.06	0.06	-0.02	0.04	0.15	0.06	0.02
m-CH_3	-	-	--	-	-	-	0	0.09	0.02	0
p-CH_3	0.04	0.04	0.15	0.01	0	-0.07	0.10	0.04	0.03	0.05
p-OCH_3	0.08	0.02	0.19	0.05	0	-0.07	0.12	0.03	0.02	0

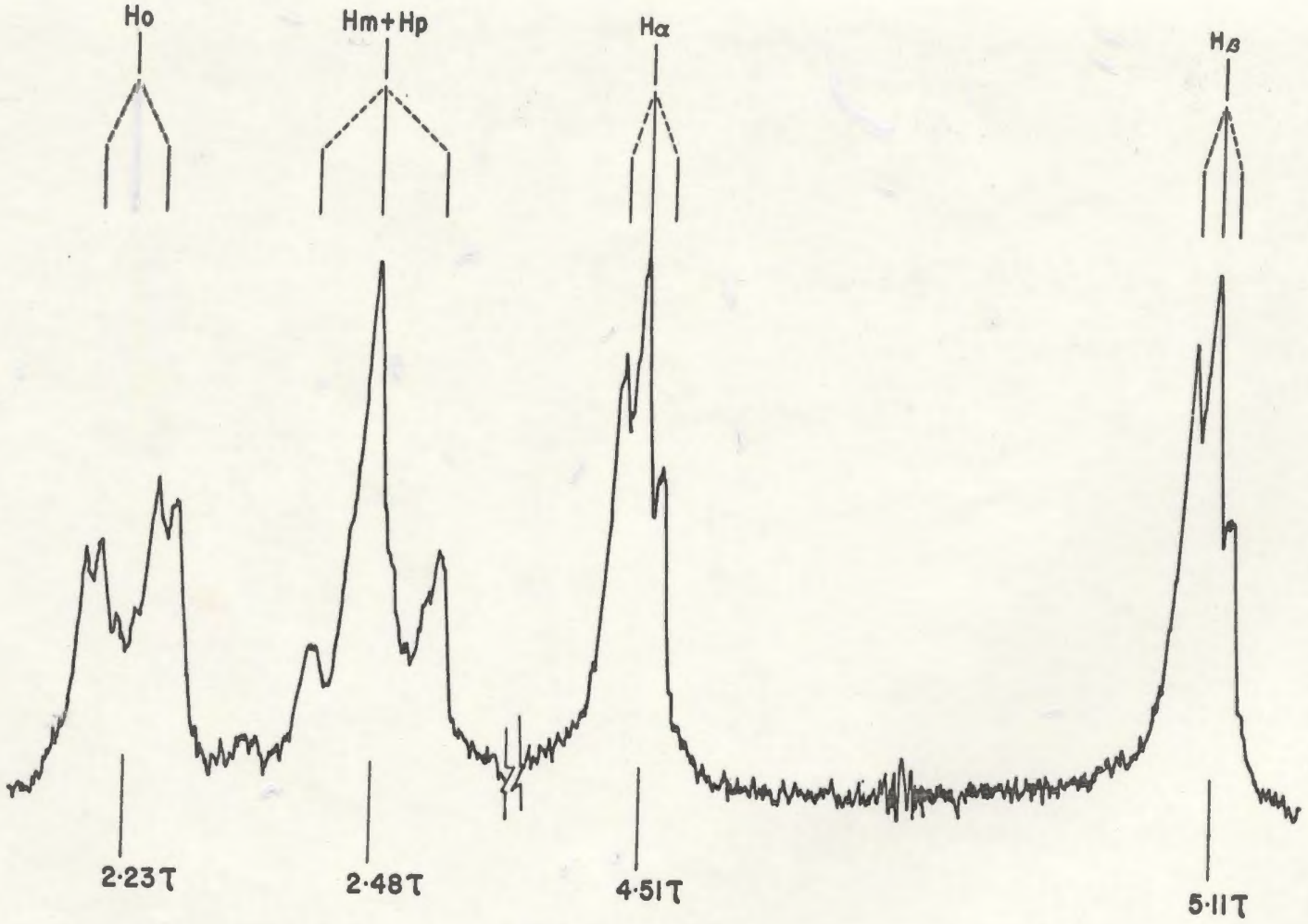
The spectrum of $C_6H_5COC_5H_4Mn(CO)_3$ (Spectrum 5-3) shows, apart from the two triplets at higher fields due to the cyclopentadienyl protons, a doublet of doublets centred at 2.23 τ and two triplets at about 2.47 τ of intensity ratio 2:3. They are assigned as indicated and the observed coupling constants are J_{ortho} = 7.5 cps; J_{meta} = 1.8 cps.

Generally, mono-substituted benzenes having an electron-withdrawing group such as CO show well resolved signals. Di-substituted analogues are often more complex except perhaps para-di-substituted benzenes which can be analysed as AA'BB' systems[28]. In systems considered here, the J_{ortho} values are very much higher than those of J_{meta} and J_{para}. As such the para di-substituted benzenes approach an AB type system and have been considered accordingly.

Substituent Effects on Arene Proton Resonances.

The substituent effects on the arene proton resonances are summarised in Table 5-4. The arene protons in the table are named with respect to the position of the ketonic carbonyl group.

In the para-di-substituted derivatives, the para substituent shifts the ortho (meta to itself) proton resonances downfield and the meta (ortho to itself) proton resonances upfield in the order, OCH_3 > F > CH_3 ≈ H ≈ Cl (Table 5-4). The former shift is probably due to the



Spectrum 5-3

NMR Spectrum of $C_6H_5COC_5H_4Mn(CO)_3$ in $CDCl_3$

TABLE 5-4

NMR Spectral Data of Arene Ring Protons of Some

$XC_6H_4COC_5H_3YMn(CO)_3$ Complexes

X	Y = H				Y = α-CH_3				Y = β-CH_3			
	H_o	H_p	H_m	H(X)	H_o	H_p	$H_m(H_{m'})$	H(X)	H_o	H_p	$H_m(H_{m'})$	H(X)
H	2.23	2.47	2.49	-	2.19	2.47	2.43	-	2.26	2.51	2.50	-
o-CH_3	'multiplets at 2.73'			7.59	'multiplets at 2.75'			7.61	'multiplets at 2.73'			7.60
o-Cl	'singlet at 2.62'			-	'multiplets at 2.63'			-	'multiplets at 2.63'			-
o-F	2.53(m)	-	2.80(m)	-	-	-	-	-	-	-	-	-
o-OH	-	-	-	-	-	-	-	-	2.20	2.54	3.00 (3.12)	-
m-CH_3	2.44(m)	2.64(m)		7.59	2.45(m)	2.65(m)		-	2.45(m)	2.65(m)		7.57

(continued)

TABLE 5-4 (continued)

NMR Spectral Data of Arene Ring Protons of Some

$XC_6H_4COC_5H_3YMn(CO)_3$ Complexes

X	Y = H				Y = α-CH_3				Y = β-CH_3			
	H_o	H_p	H_m	H(X)	H_o	H_p	$H_m(H_{m'})$	H(X)	H_o	H_p	$H_m(H_{m'})$	H(X)
m-F	2.51(m)	2.61(m)	2.68(m)	-	2.52(m)	2.62(m)	2.70(m)	-	-	-	-	-
p-CH_3	2.32	-	2.76	7.60	2.28	-	2.72	7.59	2.33	2.76	2.76	7.60
p-Cl	2.28	-	2.58	-	2.31	-	2.59	-	2.31	-	2.59	-
p-F	2.19	-	2.87	-	-	-	-	-	2.22	-	2.89	-
p-OCH_3	2.18	-	3.06	6.15	2.19	-	3.07	6.14	2.20	-	3.07	6.15

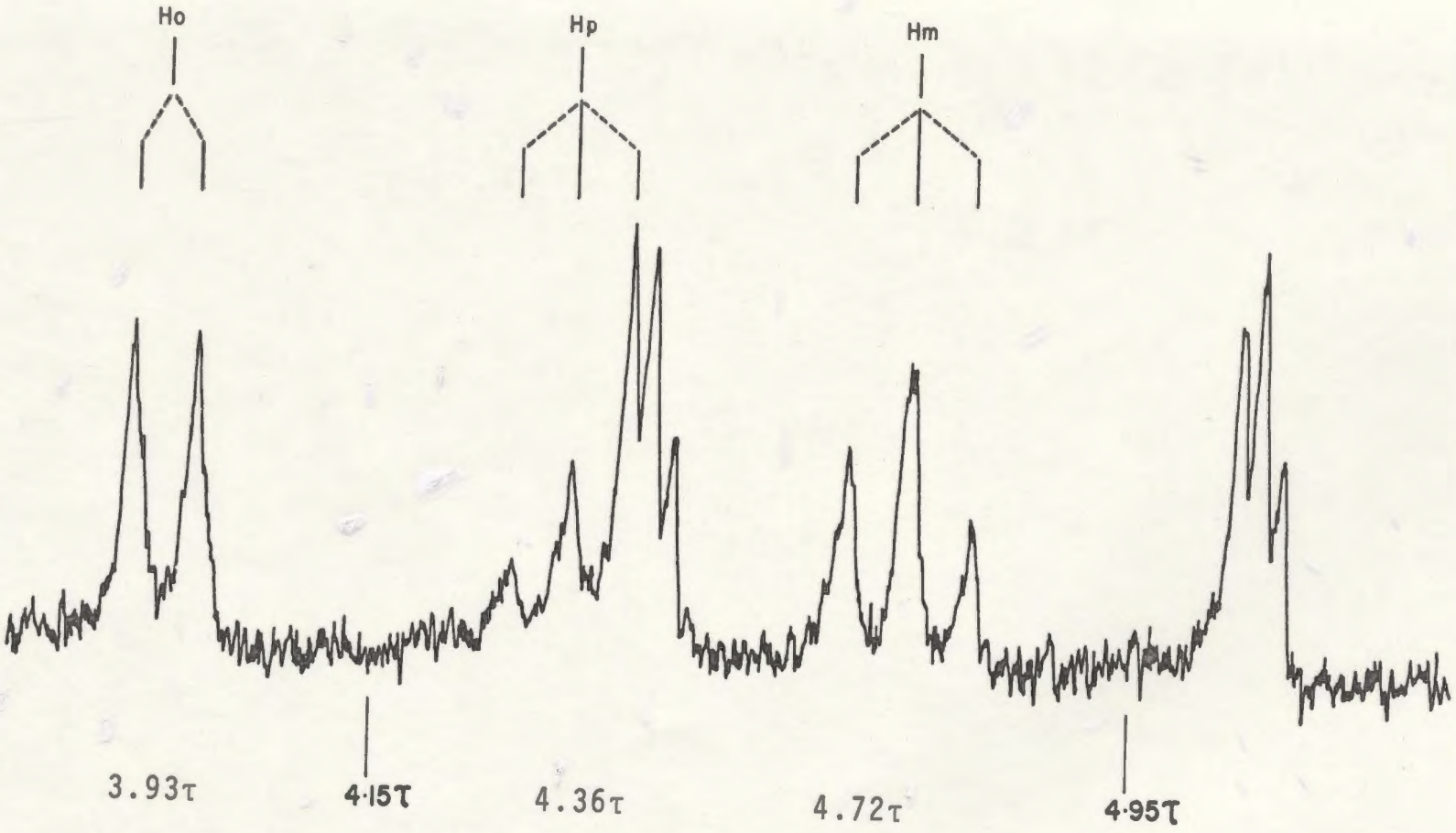
inductive effect of the substituents while the latter can be explained by the π-electron donating ability of the substituents. It appears that the proton resonances of the methyl protons on the arene ring are not affected regardless of the position of substitution.

Arene Proton Resonances of π-$Cr(CO)_3$ Complexes.

The most significant feature of spectra of these π-complexes is the upfield shift of the aromatic ring protons. The proton resonance signals of the compound before complexing with the $Cr(CO)_3$ group are often observed as multiplets and difficult to assign (Spectrum 5-3). This is not so in the π-$Cr(CO)_3$ complexes. The spectrum of $[(CO)_3Cr]C_6H_5COC_5H_4Mn(CO)_3$ for example, shows a doublet at 3.93 τ, a triplet at 4.36 τ and another triplet at 4.72 τ of intensity ratio 2:1:2, (Spectrum 5-4). These are correspondingly assigned to the ortho, para, and meta protons. The proton coupling constants are J_{ortho} = 6.5 cps, J_{meta} = 1.2 cps. (Table 5-5).

Substituent Effects on Arene Proton Resonances of π-$Cr(CO)_3$ Complexes.

As previously shown, the substituent $-COC_5H_4Mn(CO)_3$ is strongly electron-withdrawing and tends to reduce the electron density at the ortho and para protons. Correspondingly, a downfield shift is expected for these proton



Spectrum 5-4

NMR Spectrum of $[(CO)_3Cr]C_6H_5COC_5H_4Mn(CO)_3$ in $CDCl_3$

TABLE 5-5

NMR Spectral Data of Arene Ring Protons of Some

$[(CO)_3Cr]XC_6H_4COC_5H_3YMn(CO)_3$ Complexes ($\tau \pm 0.001$ ppm)

X	Y = H				Y = α-CH_3				Y = β-CH_3			
	$H_o(H_{o'})$	H_p	$H_m(H_{m'})$	H(X)	$H_o(H_{o'})$	H_p	$H_m(H_{m'})$	H(X)	$H_o(H_{o'})$	H_p	$H_m(H_{m'})$	H(X)
H	3.93	4.36	4.72	-	3.93	4.37	4.73	-	3.95	4.37	4.72	-
o-CH_3	4.30	4.49	4.87 (4.89)	7.69	4.39	4.52	4.88 (4.87)	7.75	4.32	4.55	4.85 (4.60)	7.70
m-CH_3	4.09 (4.12)	4.48	4.65	7.75	-	-	-	-	4.14 (4.11)	4.60	4.66	7.75
p-CH_3	3.89	-	4.86	7.69	3.89	-	4.88	7.70	3.91	-	4.85	7.70
p-OCH_3	3.79	-	4.85	6.23	3.81	-	4.84	6.23	3.80	-	4.85	6.23

resonances; whereas, the meta proton resonances are expected to be almost unaffected. This has been supported by the results obtained by Mangini and Taddei[26] in their studies of mono-substituted benzenechromium tricarbonyl complexes.

If Ω is the difference between the ring proton resonance in ppm before substitution in the free ligand (or complex) and after substitution, then it is a measure of the perturbation of the substituent on the ligand (or complex). Consider, for example, the effect of the substituent, $-COC_5H_4Mn(CO)_3$, on the proton resonances of benzene and benzenechromium tricarbonyl.

C_6H_6	τ_o	τ_m	τ_p
C_6H_6	2.73	2.73	2.73
$C_6H_5COC_5H_4Mn(CO)_3$	2.23	2.49	2.47
Ω (ppm)	+0.50	+0.24	+0.26
$(CO)_3CrC_6H_6$	4.77	4.77	4.77
$[(CO)_3Cr]C_6H_5COC_5H_4Mn(CO)_3$	3.93	4.72	4.36
Ω (ppm)	+0.84	+0.05	+0.41

If Taft's argument[29] that the meta protons are mainly sensitive to the inductive effects of the substituent is assumed, then the results as shown above suggest that the

effect of the $-COC_5H_4Mn(CO)_3$ substituent as an inductive group is reduced in the π-$Cr(CO)_3$ complex. It may be suggested that the $Cr(CO)_3$ group decreases the σ-character of the benzene ring which is in agreement with the results obtained by McFarlane and Grim[14], Gubin et al.[16] and Emanual and Randall[24]. Perhaps the benzene ring carbon atoms undergo a rehybridisation from sp^2 to a slightly more saturated configuration. This is supported by the infrared studies which show that the C-C stretching frequencies of the benzene ring is lowered on complexing with the $Cr(CO)_3$ group (Chapter 3). A similar conclusion has been suggested by Mann[30] who observed that the ^{13}C resonance of the arene ligand is shifted upfield when the latter is complexed with a $Cr(CO)_3$ group.

The values also suggest that the conjugative π--effect of the substituent, $-COC_5H_4Mn(CO)_3$ on the π-$Cr(CO)_3$ complex is not reduced but rather enhanced as compared to that of the uncomplexed compound. This may be interpreted as an increase in π-electron delocalisation in the whole molecule when the arene ring is π-complexed with a $Cr(CO)_3$ group.

Upfield Shift of Arene Proton Resonances.

The results are summarised in Table 5-6. The perturbation of the $Cr(CO)_3$ group on the arene proton resonances, ΔH, is defined by ΔH (ppm) = H (after complexing) - H (before complexing). Hence, a positive value of ΔH

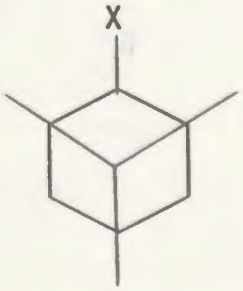
TABLE 5-6

Perturbation of the Arene Proton Resonances by the $Cr(CO)_3$ Moiety of Some $[(CO)_3Cr]XC_6H_4COC_5H_3YMn(CO)_3$ Complexes

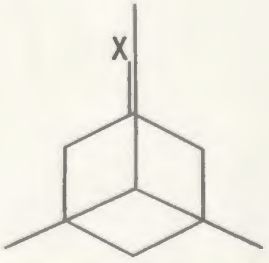
X	Y = H				Y = α-CH_3				Y = β-CH_3			
	ΔH_o	ΔH_p	ΔH_m	$\Delta H(X)$	ΔH_o	ΔH_p	ΔH_m	$\Delta H(X)$	ΔH_o	ΔH_p	ΔH_m	$\Delta H(X)$
H	1.70	1.89	2.23	-	1.74	1.90	2.30	-	1.69	1.86	2.22	-
o-CH_3	1.57	1.76	2.14 (2.16	0.10	1.84	1.77	2.13 (2.12)	0.14	1.59	1.82	2.12 (1.87)	0.10
m-CH_3	1.65 (1.68)	1.84	2.01	0.16	-	-	-	-	1.66 (1.69)	1.95	2.01	0.18
p-CH_3	1.57	-	2.10	0.09	1.61	-	2.16	0.11	1.58	-	2.09	0.10
p-OCH_3	1.61	-	1.79	0.08	1.62	-	1.77	0.09	1.60	-	1.78	0.08

means an upfield shift of the arene proton resonances when the arene ring is complexed with $Cr(CO)_3$. The value of ΔH_m (ca. 2 ppm) for the meta proton resonance is of the same order of upfield shift observed for benzene and benzenechromium tricarbonyl protons (2.04 ppm). The ΔH_o and ΔH_p values, however, are smaller, which is expected if it is assumed that the π-conjugative effect of the aromatic ring is not reduced in the $Cr(CO)_3$ complex.

It is not surprising that free rotation of the $Cr(CO)_3$ group about the ring in a large molecule like $[(CO)_3Cr]C_6H_5COC_5H_4Mn(CO)_3$, is very much restricted and the $Cr(CO)_3$ may be 'locked' in some preferred conformation shown below.



conformer (a)



conformer (b)

The bonding model for arenechromium tricarbonyl, as proposed by Carter et al.[31], shows that conformer (a) is more stable if the substituent is electron-withdrawing. On such a basis and the fact that conformer (b) is sterically less favourable, it is suggested that conformer (a) is more favoured in the system considered here. Such a

conformation is consistent with the results observed in Table 5-6. The low values of ΔH_o and ΔH_p may then be attributed to the magnetic anisotropy of the $Cr(CO)_3$ moiety which affects the various arene proton resonances differently. Apparently, the upfield shift is less for ring protons eclipsed with the CO ligands of the $Cr(CO)_3$ group (ortho and para protons), than for the other ring protons (meta protons).

Proton Coupling Constants

The proton-proton coupling constants of the arene ring before complexing with a $Cr(CO)_3$ group are found to be J_{ortho} = 7.5 - 8.5 cps; J_{meta} = 1.4 - 2.0 cps; and J_{para} < 0.5 cps. After the arene ring was complexed with $Cr(CO)_3$, the coupling constants are found to be reduced J_{ortho} = 6.0 - 6.5 cps; J_{meta} = 1.0 - 1.5 cps; J_{para} < 0.1 cps. It is difficult to explain this reduction in coupling constants of the π-$Cr(CO)_3$ complex but a rehybridisation of the arene carbon atoms from sp^2 to a more saturated configuration certainly decreases the amount of s-character in the arene protons and such a possibility cannot be ruled out.

Spectra of Miscellaneous Complexes.

The spectra of some non-conjugated systems and systems not conjugated via a ketonic CO group have also been studied. The arene proton resonance signals are usually

observed as narrow multiplets, (Table 5-7), which suggest that the arene protons are not significantly perturbed by the substituent. The arene proton resonances of complexes with R = C_6H_5- and R = $CH{=}CHC_6H_5$ are, however, found at slightly lower field than non-conjugated substituents. The proton resonances of the π-$Cr(CO)_3$ complexes are again found at higher field but no differential magnetic anisotropy is observed, at least not on an NMR time scale.

The cyclopentadienyl proton resonance signals are all shifted to lower field after complexing with $Cr(CO)_3$, except where R = C_6H_5 in which an upfield shift of ca. 0.12 ppm is observed. Perhaps the α-positions of the cyclopentadienyl ring lie within the anisotropic field of the $Cr(CO)_3$ moiety which has an upfield effect. This is further evident from the upfield shifts observed in the methylene protons and one of the methine protons of complexes having R = $CH_2C_6H_5$ and R = $CH{=}CHC_6H_5$ respectively. The -CH=CH- group of the latter constitutes an AB system with J_{HH} = 17 cps. This corresponds more to a trans- than cis-configuration.

TABLE 5-7

NMR Spectral Data of Some Complexes of the Type R-$C_5H_4Mn(CO)_3$ ($\tau \pm 0.005$ ppm)

R	H(phenyl)	H_α	H_β	Miscellaneous
H-	-	5.28	5.28	
C_6H_5-	2.67(m)	4.83	5.24	$H(CH_2)$ = 6.42
$C_6H_5CH_2$-	2.74(s)	5.38	5.38	$H(CH_2)$ = 6.12
$C_6H_5CH_2CO$-	2.72(s)	4.60	5.22	$H(CH_2)$ = 7.07; H(CH) = 8.15; H(OH) = 5.13
$C_6H_5CH_2CH(OH)$-	2.75(s)	5.39	5.39	H(CH= CH) = 6.81, 5.57
C_6H_5CH= CH-	2.67(m)	5.03	5.30	
$(CO)_3CrC_6H_5$-	4.66, 4.74	4.95	5.23	$H(CH_2)$ = 6.63
$(CO)_3CrC_6H_5CH_2$-	4.78(m)	5.28	5.28	$H(CH_2)$ = 6.37
$(CO)_3CrC_6H_5CH_2CO$-	4.68(m)	4.50	5.07	$H(CH_2)$ = 7.33
$(CO)_3CrC_6H_5CH_2CH(OH)$-	4.70(m)	5.29	5.29	
$(CO)_3CrC_6H_5CH$= CH-	4.40(m)	4.77	5.10	

TABLE 5-7

NMR Spectral Data of Some Complexes of the Type R-$C_5H_4Mn(CO)_3$ ($\tau \pm 0.005$ ppm)

R	H(phenyl)	H_α	H_β	Miscellaneous
H-	-	5.28	5.28	
C_6H_5-	2.67(m)	4.83	5.24	
$C_6H_5CH_2$-	2.74(s)	5.38	5.38	$H(CH_2)$ = 6.42
$C_6H_5CH_2CO$-	2.72(s)	4.60	5.22	$H(CH_2)$ = 6.12
$C_6H_5CH_2CH(OH)$-	2.75(s)	5.39	5.39	$H(CH_2)$ = 7.07; H(CH) = 8.15; H(OH) = 5.13
$C_6H_5CH{=}CH$-	2.67(m)	5.03	5.30	H(CH=CH) = 3.19, 3.43
$(CO)_3CrC_6H_5$-	4.66, 4.74	4.95	5.23	
$(CO)_3CrC_6H_5CH_2$-	4.78(m)	5.28	5.28	$H(CH_2)$ = 6.63
$(CO)_3CrC_6H_5CH_2CO$-	4.68(m)	4.50	5.07	$H(CH_2)$ = 6.37
$(CO)_3CrC_6H_5CH_2CH(OH)$-	4.70(m)	5.29	5.29	$H(CH_2)$ = 7.33
$(CO)_3CrC_6H_5CH{=}CH$-	4.40(m)	4.77	5.10	H(CH=CH) = 2.25(s), 3.35(d)

EXPERIMENTAL

The NMR spectra were recorded with a Varian Model HA 100 Spectrometer operating at 100 Mc/s. The solutions were prepared using $CDCl_3$ as solvent and concentrations between 0.02 and 0.05 M, were used. The spectral signals were calibrated with TMS as internal reference and locking signal. In cases where multiplets were observed, the spectra were scanned at 250 cps sweep-width.

CONCLUSION

The NMR spectral analysis of $C_5H_5Mn(CO)_3$ derivatives shows that the α- and β-proton resonances are shifted to lower fields when the substituent is C_6H_5CO-. The α-protons are more sensitive to electronic changes of this substituent than the β-protons. These observations are interpreted in terms of conjugative effects rather than inductive effects as proposed by Slocum and Ernst[10] for derivatives of ferrocenes.

The results obtained in this study agree with those of previous workers that although the $Cr(CO)_3$ group is essentially withdrawing π-electron density from the arene ring, the π-conjugative effect of the ring in these complexes is not reduced. Furthermore, a corresponding

change in the inductive effect is observed.

It is believed that the upfield shift of the arene proton resonances in these complexes is dependent on several factors. These include withdrawal of π-electron density from the ring thereby reducing the ring current and at the same time increasing the electronegativity of the σ-framework of the ring; magnetic anisotropy of the $Cr(CO)_3$ moiety; and perhaps a rehybridisation of the carbon atomic orbitals to higher saturation.

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CHAPTER 6

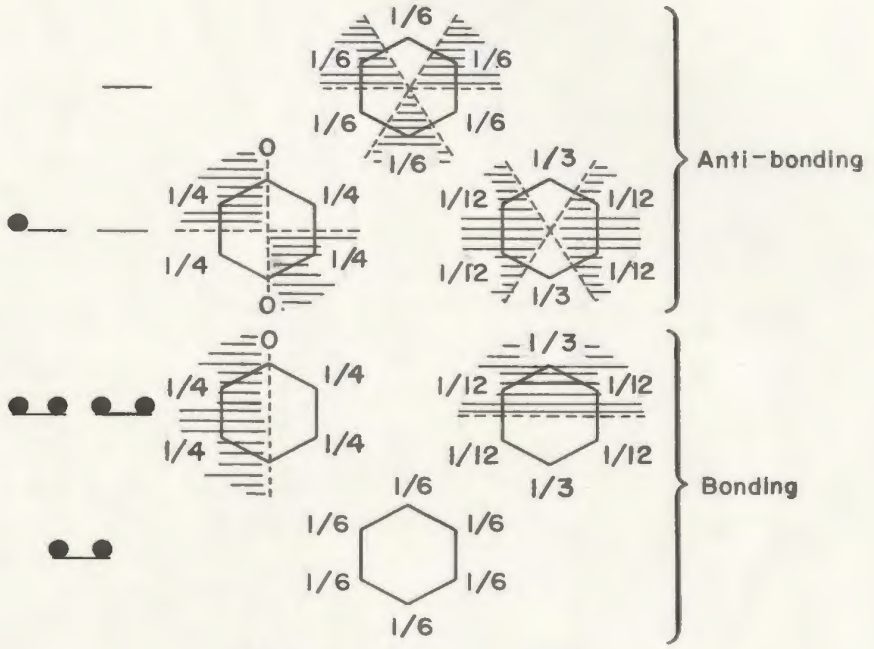
ELECTRON SPIN RESONANCE SPECTROSCOPY

INTRODUCTION

Electron Spin Resonance Spectroscopy (ESR) sometimes known as Electron Paramagnetic Resonance Spectroscopy (EPR), is an important technique for the investigation of electronic structures and kinetic studies of systems which have a net electron angular momentum. These include free radicals, triplet state systems, most transition-metal ions and point defects in solids.

The ESR studies of π-type radicals are best illustrated by considering the spectrum of the benzene radical anion produced by alkali metal reduction[1]. Seven hyperfine lines of relative intensities 1:6:15:20:15:6:1 are observed at 210°K, each separated by 3.75G. McConnell[2,3] found that, for π-type organic radicals, the hyperfine splitting due to the proton is proportional to the unpaired-electron density at the adjacent carbon atom i.e. $A_H = Q\rho_C$, where A_H is the proton hyperfine splitting constant, ρ_C is the unpaired-electron density on the carbon atom and Q is a proportionality constant of magnitude between -20 and -30G. Application of this relationship to the spectrum of the benzene radical anion shows that the average probability of finding the unpaired electron in the vicinity of any one carbon atom is the same. This can be explained by the simple Hückel

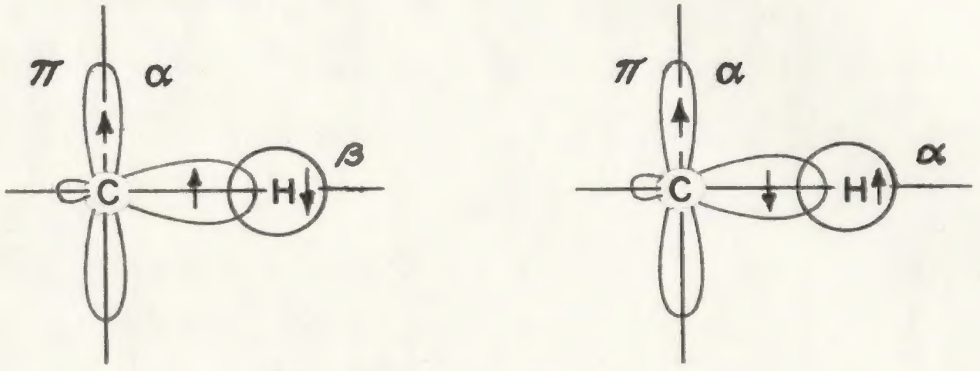
molecular orbital (HMO) theory[4] which assumes that the six π-electrons occupy orbitals formed by linear combination of the carbon $2p_z$ atomic orbitals. The extra electron of the benzene anion can occupy either of the two e_2 antibonding molecular orbitals with equal probability.



The average unpaired electron density at a given position is obtained by taking the average of the sum of the electron densities for each of the orbitals.

The HMO theory is not able to account for the negative spin density observed in anions of some π-systems, notably the pyrene negative ion[5]. This is because the HMO theory assumes that, apart from the unpaired electron,

all other electrons are completely paired. This is not quite true because the unpaired electron is capable of unpairing, to a slight extent, the other π-electrons, a phenomenon commonly known as spin-polarisation.

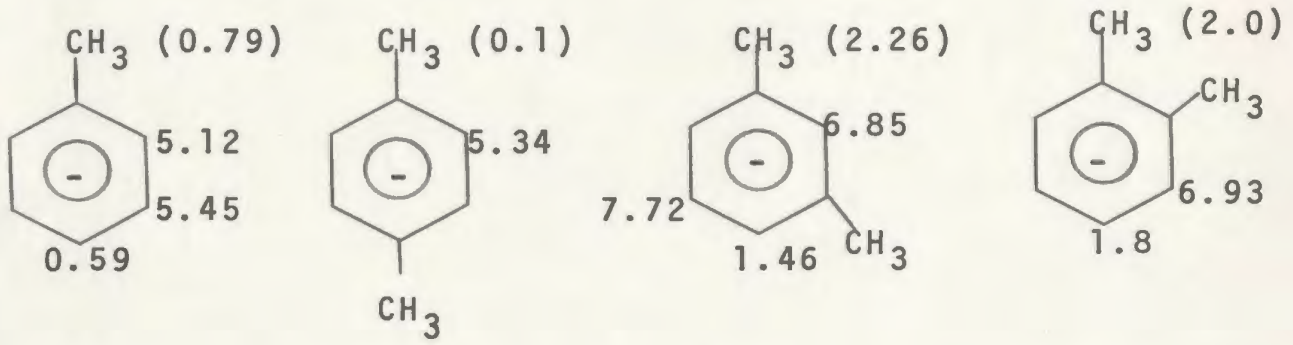


(a) (b)

Consider the unpaired electron in the π-orbital to have a positive spin α. If this unpaired electron is absent then the probability of configuration (a) and (b) are the same. However, if we include this unpaired electron then Hund's rule favours configuration (a). As a result the spin on the proton is preferentially negative. This phenomenon of negative spin has been demonstrated by NMR studies of the biphenyl anion[6]. The HMO theory can be extended to take into account interactions of all π-electrons.

This can be done in several ways, of which the approximate configuration-interaction treatment of McLachlan[7,8] has been very popular.

The introduction of any substituent into the conjugated system will tend to remove the degeneracy of the symmetric and anti-symmetric e_2 molecular orbitals. The unpaired electron will occupy whichever is the more stable. This concept is only true if the effect of the substituent is small, i.e. it does not produce a large perturbation on the orbital wave function. The methyl substituent, for example, is electron repelling and will tend to destabilise the symmetrical orbital thus facilitating occupation of the anti-symmetric orbital by the unpaired electron. Carrington and Bolton[9] obtained good agreement between calculated and experimental results of some alkyl-substituted benzene anions. The observed hyperfine splittings are given below.



(A) (A) (S) (S)

A and S notations signify anti-symmetric and symmetric orbitals respectively.

Rieger and Fraenkel[10] applied the extended HMO-McLachlan theory to some aromatic anions containing electron-attracting substituents like CN and CO. They have been able to obtain improved agreement between calculated spin densities and experimental results. Furthermore, a correlation between electron-withdrawing effects and the magnitude of the ring-proton splittings is obtained. For example, the proton splitting of the anion radical 1,4-dinitrobenzene is -1.12G while that of 1,4-diacetylbenzene is +1.33G. This is consistent with the electron-withdrawing affinity of the substituents which decreases in the order nitro > cyano > acetyl ∿ aldehyde.

Though some detailed electrochemical studies of organometallic radical anions and their ESR have been carried out by Dessy and co-workers[11,4], very few radical anions of metal carbonyls have been reported. Elschenbroich and Cais[12] were among the first to carry out systematic ESR studies of ferrocene-substituted radical anions. Hyperfine splittings attributed to the para and ortho protons of the phenyl ring have been observed but no such splittings can be assigned to the cyclopentadienyl protons. This suggests that the unpaired electron in benzoylferrocene anion appears to reside more on the phenyl ring than on the ferrocene moiety. This is substantiated by HMO

calculations[13] which also show that a large fraction of the spin density is found on nuclei which do not contribute to the observed splittings. This is evident from the much smaller total width of the spectrum of the benzoylferrocene anion (13.66G) as compared to that of benzophenone (24.5G).

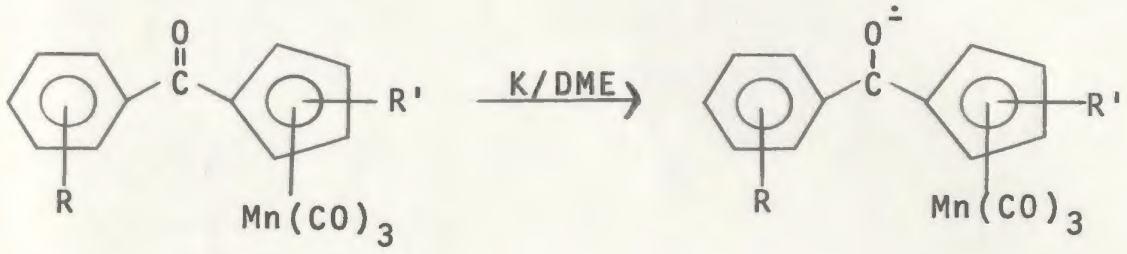
A similar study has also been carried out by Bigam et al.[14]. It is suggested that the increase in the g--value when the phenyl group of benzoylferrocene is replaced by a t-butyl group is evidence that there is a significant participation of iron orbitals in the π-system. The results observed are not direct proof that the iron orbitals in ferrocene derivatives are involved in the π-bonding. Benzoylruthenocene anion for example[15], has a g-value of 2.0035 which is close to that of the benzophenone anion (2.0036), an observation which can be interpreted to imply insignificant interaction of metal orbitals with the π-system. Yet the proton hyperfine splittings in the benzoylruthenocene anion are almost identical with those of the benzoylferrocene anion.

The reason for the controversy is that the central metal atom has zero nuclear spin and gives no direct observable couplings. It has been shown in the present study that such a dilemma does not exist in benzoylcyclopentadienylmanganese tricarbonyl derivatives[16] where the

central manganese atom has a nuclear spin of 5/2. Six hyperfine lines have been observed which is direct proof that the orbitals of the manganese atom are significantly participating with the π-system of the molecule; the magnitude of these coupling constants (A_{Mn}) is a measure of the amount of spin localisation on the metal.

RESULTS AND DISCUSSION

The radical anions were generated by alkali metal (potassium) reduction of the ketones in dimethoxyethane as solvent.



It has been shown[12] that the reduction takes place at the ketonic carbonyl of the molecule and the process can be visualised as the potassium atom contributing its single valence electron to the π-system of the ketonic carbonyl. This unpaired electron is then delocalised over the complete molecule. The average probability of its residence at each atom of the molecule is measured by the interactions of the nuclear magnetic moments of the atoms with this unpaired spin.

The spectra are interpreted using the spin Hamiltonian

$$H = g\beta H.S + \sum_i A_i I_i.S$$

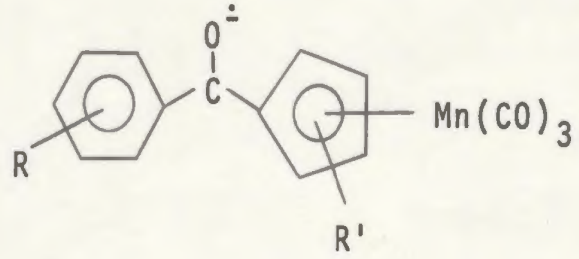
where A_i is the hyperfine constant for the $i^{\underline{th}}$ nucleus of nuclear spin I_i. The resonant magnetic fields can be

obtained either by diagonalising the Hamiltonian or by perturbation. In these systems, the second order perturbation calculations yield satisfactory results. The results are as shown in Table 6-1.

Spectra are obtained at temperatures between -100° to room temperature. At temperatures below -70° the concentrated solutions often show anisotropy and all the three g-values are observed. As the temperature is increased from -70°, six broad lines are observable. The intensity of these lines increases with temperature and the two wing lines are much stronger than the other four. However, no resolved spectrum is observed. The solution is diluted until well resolved hyperfine lines are obtained, but in most cases the wings are still more intense than the other lines. This phenomenon may be attributed to dipolar interactions and is very difficult to remedy without significant loss of signal/noise ratio. The radical anions appear as deep purple solutions but if allowed to stand over excess potassium in the presence of light, they turn reddish purple and finally deep red. The spectrum shows six lines when purple but an independent broad line soon appears between the six Mn^{55} lines. Its intensity increases with time and at the expense of the six Mn^{55} lines until finally only one broad band is observed. When allowed to stand, the solution develops a deep red coloration and no ESR

TABLE 6-1

ESR Spectral Data of Some π-Radical Anions of The Type



Radical Anions			Hyperfine splitting constants (gauss)					
	R	R'	A_{Mn}	$A_{H(para)}$	$A_{H(ortho)}$	$A_{H(CH_3)}$	line-width	g
I	H	H	7.67 ± 0.02	2.91 ± 0.02	1.03 ± 0.01		0.5	2.0001
II	H	α-CH_3	6.16 ± 0.05	3.46 ± 0.02	0.85 ± 0.01		0.5	1.9998
III	H	β-CH_3	7.77 ± 0.06	3.00 ± 0.02	1.04 ± 0.02		0.6	2.0001
IV	o-CH_3	H	11.81 ± 0.02				3.7	1.9990
V	o-CH_3	α-CH_3	11.98 ± 0.02				3.8	1.9985
VI	m-CH_3	H	8.10 ± 0.03				3.9	1.9997
VII	m-CH_3	α-CH_3	7.95 ± 0.02				3.6	1.9997
VIII	m-CH_3	β-CH_3	8.17 ± 0.02				4.0	1.9999

TABLE 6-1(continued)

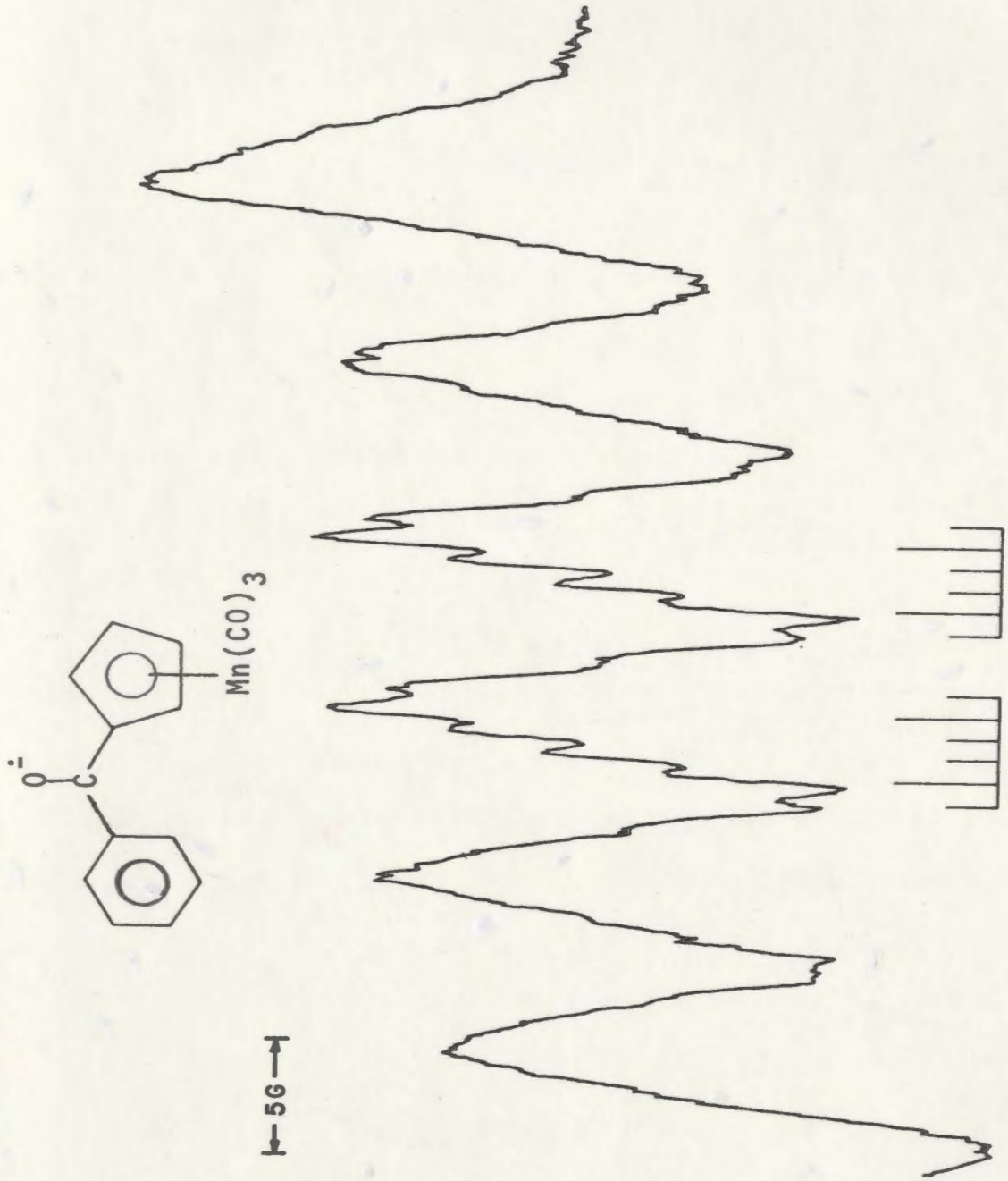
	Radical Anions		Hyperfine splitting constants (gauss)					
	R	R'	A_{Mn}	$A_{H(para)}$	$A_{H(ortho)}$	$A_{H(CH_3)}$	line-width	g
IX	p-CH_3	H	9.02 ± 0.03				4.7	1.9992
X	p-CH_3	α-CH_3	7.73 ± 0.02		0.90 ± 0.02	2.60 ± 0.02	1.5	1.9995
XI	p-CH_3	β-CH_3	9.05 ± 0.03			2.41 ± 0.04	-	1.9996
XII	p-OCH_3	H	10.55 ± 0.03				4.5	1.9989
XIII	p-OCH_3	α-CH_3	10.44 ± 0.02				4.1	1.9985
XIV	p-OCH_3	β-CH_3	10.66 ± 0.03				4.7	1.9990
XV	o-Cl	H	7.32 ± 0.02				2.8	2.0026
XVI	o-Cl	α-CH_3	One Broad Band				3.4	2.0028
XVII	o-Cl	β-CH_3	7.22 ± 0.03				2.5	2.0031

signal can then be detected. These observations suggest that perhaps the radical anion formed by the one electron reduction process is capable of participating with excess potassium to form a paramagnetic ion pair. Further reduction by potassium gives a diamagnetic dinegative anion.

$$X^{\cdot-} + K \longrightarrow \underset{\text{(ion-pair)}}{[K - X]^{\cdot-}} \longrightarrow \underset{\text{(dinegative anion)}}{K^{+} + X^{--}}$$

The spectra of these radical anions generally show a six-line pattern due to the Mn^{55} nuclei (I = 5/2) interacting with the unpaired electron. Each of these lines is split by the phenyl ring protons. The radical anion of (I), for example, shows six Mn^{55} lines separated by a width of 7.67G. This is further split into a doublet of triplets as shown in Spectrum 6-1. Only the two central lines are well resolved whereas the broadened end lines may be attributed to dipolar interaction.

The spectra of radical anions (I), (II), and (III) have been previously interpreted[16] and shown in Table 6-1. The doublets and triplets have been assigned to the splittings of the para and ortho protons respectively. These assignments are further confirmed by isotopic studies in which the phenyl protons of the radical anions are completely replaced by deuterium atoms. Six lines



Spectrum 6-1. ESR Spectrum of Radical Anion I.

having line-widths of 2.5G are observed but no hyperfines of the cyclopentadienyl protons have been observed. These results imply that a large fraction of the unpaired electron resides on the manganese atom and that delocalisation on the phenyl ring is more important than on the cyclopentadienyl ring. This supports the observation that $C_5H_5Mn(CO)_3$ is more readily attacked by electrophilic agents than benzene[17]. These are in agreement with the assignment proposed by Elschenbroich and Cais[12] for benzoylferrocene radical anion. The same conclusion has been derived by Bigam et al.[14], McDonnell and Pochopien[18], and McEwen et al.[19].

The methyl group at the β-position of the cyclopentadienyl ring as seen in radical anion III, does not seem to cause the Mn^{55} splitting constant to differ very much from that of radical anion I. Substitution of the methyl group on the α-position of the cyclopentadienyl ring, however, shows a significant decrease in this value. This may be explained via the electron repelling tendency of the methyl group which makes it less favourable for the lone electron to be delocalised in the $-C_5H_4Mn(CO)_3$ system. There is another factor which may contribute to this phenomenon. The α-methyl group is capable of hindering the overlapping of the pπ orbitals of the ketonic CO with the π-molecular orbitals of the $-C_5H_4Mn(CO)_3$ system. Consequently, the delocalisation of the unpaired

electron on the manganese atom is reduced with concomitant increase in the phenyl proton splitting constants.

Table 6-1 shows the data obtained from the spectra of radical anions I - XVII. The A_{Mn} values are observed to change with substituents on the arene ring. The order of decreasing A_{Mn} values appear to be o-CH_3 > p-OCH_3 > p-CH_3 > m-CH_3 ∿ H > o-Cl. This trend is in good agreement with the argument proposed previously to explain the effect of the methyl substituent on the cyclopentadienyl ring. It is unfortunate that most of these spectra are not well resolved. This is due to the fact that the electron repelling substituents on the phenyl ring do not leave enough spin density on the ring to give coupling constants greater than the line-widths of the Mn^{55} bands. Consequently the hyperfine lines are all enveloped within these bands. It is not clear how the substituents redistribute the spin density but it cannot be assumed that they contribute only a small perturbation to the basic benzene structure. Simple HMO calculations are inadequate to explain this phenomenon because of i) non-planarity of the molecule and ii) the heteroatomic composition of the molecule.

Extended Hückel Molecular Orbital calculations (EHMO) support the conclusion and show that the spin densities on the phenyl ring are indeed reduced[13]. The theoretical and

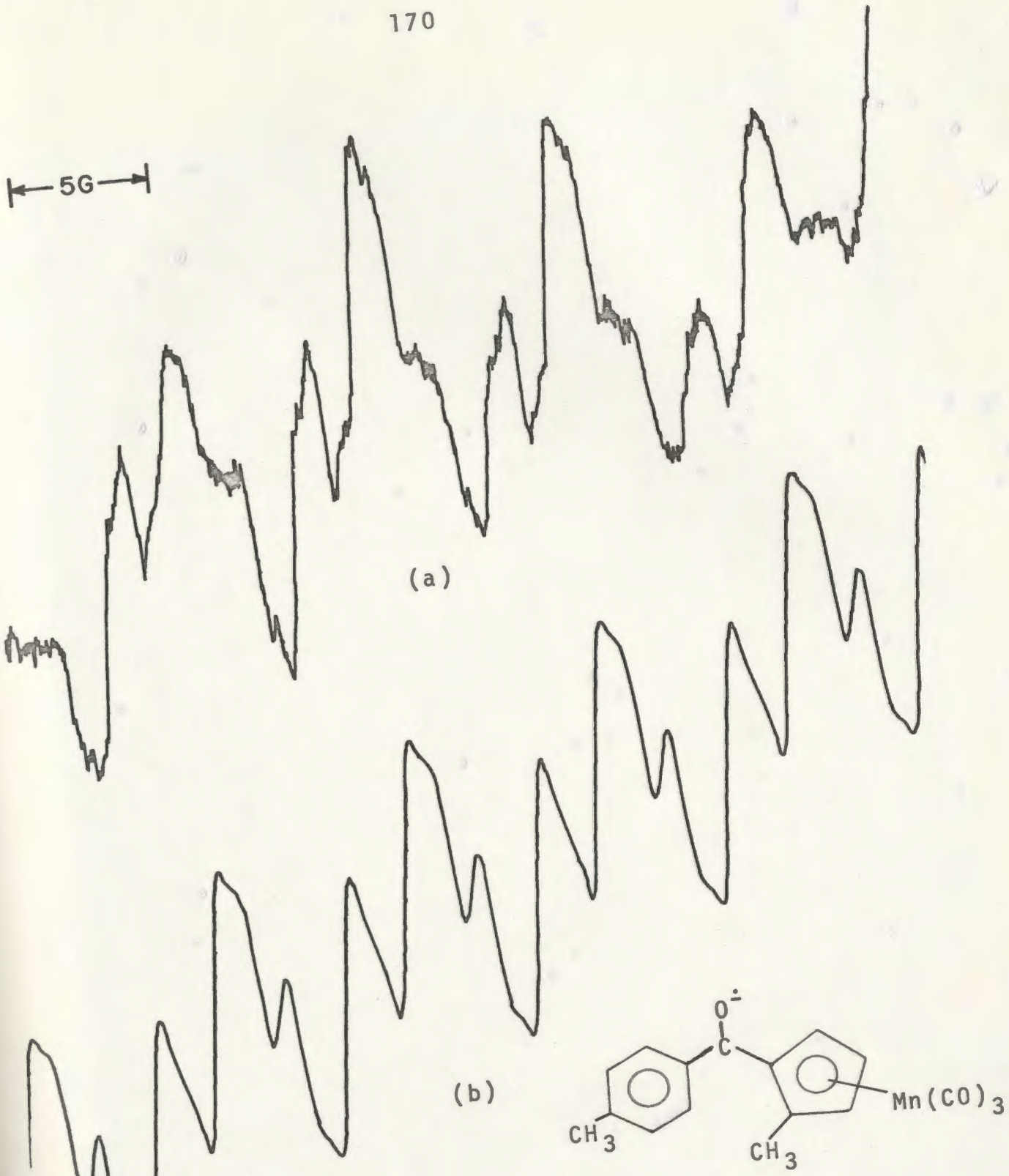
experimental spin densities are as shown in Table 6-2. Where hyperfine lines have not been observed, the upper limits of their splitting constants are estimated. The experimental spin densities are calculated using Q_C = -24G and Q_{Mn} = 38G, which are obtained from the best fit between experimental hyperfine splitting constants and theoretical spin densities. This will be further discussed in the next section.

It is also interesting to note that only the para-substituted toluylcyclopentadienylmanganese tricarbonyl (Spectrum 6-2) shows some resolved structure. The central portion of the spectrum is shown; the two wing lines are too intense and broad. The simulated spectrum shows that each Mn^{55} line is split into a quartet of triplets. The quartet is assigned to the three equivalent methyl protons whereas the triplet is assigned to the two equivalent ortho protons. The former may be visualised as a consequence of hyperconjugation in which the methyl molecular orbitals couple with the π-system of the aromatic ring. In the case of ortho-substituted toluylcyclopentadienylmanganese tricarbonyl, this methyl group is more important as a steric group than an inductive group. A molecular model shows that the methyl group tends to inhibit overlap of e_2 molecular orbitals of the phenyl ring with the pπ-orbitals of the ketonic carbonyl. Subsequently,

TABLE 6-2

Experimental and Theoretical Spin Densities for $[(C_6H_4RCOC_5H_3R'Mn(CO)_3)]^{\cdot-}$

		Experimental			Theoretical		
R	R'	ρ_{Mn}	ρ_p	ρ_o	ρ_{Mn}	ρ_p	ρ_o
H	H	0.203	0.122	0.044	0.200	0.120	0.052
H	α-CH_3	0.163	0.145	0.036	0.167	0.134	0.042
H	β-CH_3	0.205	0.126	0.044	0.203	0.120	0.046
o-CH_3	H	0.312	<0.012	<0.008	0.326	0.023	0.013
p-CH_3	H	0.238	<0.012	<0.008	0.261	0.002	0.032
o-CH_3	α-CH_3	0.316	<0.025	<0.020	0.326	0.023	0.013
p-CH_3	α-CH_3	0.204	<0.020	<0.020	0.241	0.021	0.32
p-CH_3	β-CH_3	0.239	<0.020	<0.020	0.262	0.002	0.032

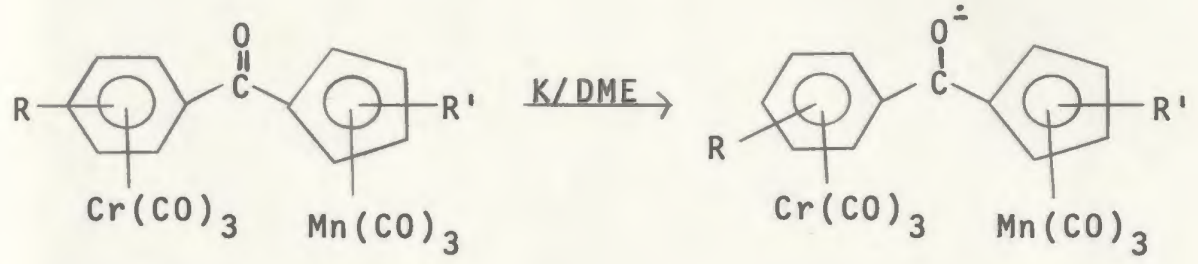


Spectrum 6-2. ESR Spectrum of Radical Anion X
(With Simulation) (Only the central lines
are shown)

the lone electron tends to reside more on the $-C_5H_4Mn(CO)_3$ system as is reflected by the high value of A_{Mn} (11.82G) of this radical anion.

Radical Anions of $[(CO)_3Cr]C_6H_5COC_5H_4Mn(CO)_3$ Derivatives.

These radical anions have been generated in a similar fashion as those previously discussed.



Solutions of these neutral complexes in DME are orange in colour and normally prepared within the concentration range of (2 - 10) x 10^{-3}M. After the reduction with potassium these solutions turn dark greenish yellow and do not give well resolved spectra. Very dilute solutions are often required. The formation of a second paramagnetic species is not so readily observed as with the radical anions of the uncomplexed species previously discussed. Only the red diamagnetic species is observed.

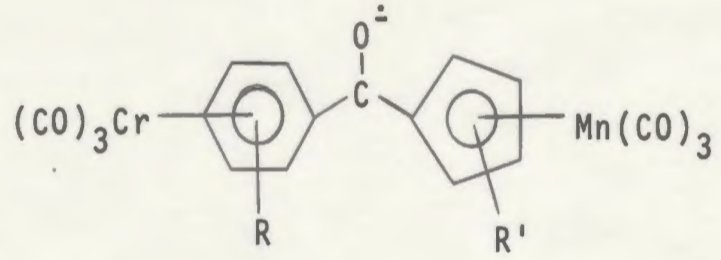
The most interesting feature of these spectra is

that the hyperfine splittings of the phenyl protons which are not observed in radical anions IV to XIV are now well defined and can be more easily assigned. This is illustrated by the spectrum of radical anion XX as seen in Spectrum 6-3a. It shows 24 lines and appears to be more intense at the wing regions. Spectrum 6-3b is a simulated spectrum showing the main features of Spectrum 6-3a and the splitting constants are as shown in Table 6-3. However, this simulation does not take into account the dipolar broadening and the two extra lines at each end of the spectrum. These extra lines are attributable to the Cr^{53} isotopes (I = 3/2) which has a natural abundance of 9.55%. By incorporating a Lorentzian curve of line-width 10.4G to account for this broadening effect a better fit is observed (Spectrum 6-3c). Spectrum 6-3d is obtained by introducing a 10% abundance of Cr^{53} to the parameters used for simulating Spectrum 6-3c. The total width of the spectrum is about 15G which is very much smaller than 43G observed for radical anion III before complexing with the $Cr(CO)_3$ group.

It is also observed that the hyperfine splitting constants of radical anion III (A_{Mn} = 7.77G, $A_{H(para)}$ = 3.00G, $A_{H(ortho)}$ = 1.04G), are all reduced drastically when the arene ring is complexed with the $Cr(CO)_3$ group (A_{Mn} = 2.52G, $A_{H(para)}$ = 1.61G, $A_{H(ortho)}$ = 0.80G). This proves that a substantial amount of spin density is withdrawn from the manganese atom onto the $Cr(CO)_3$ group.

TABLE 6-3

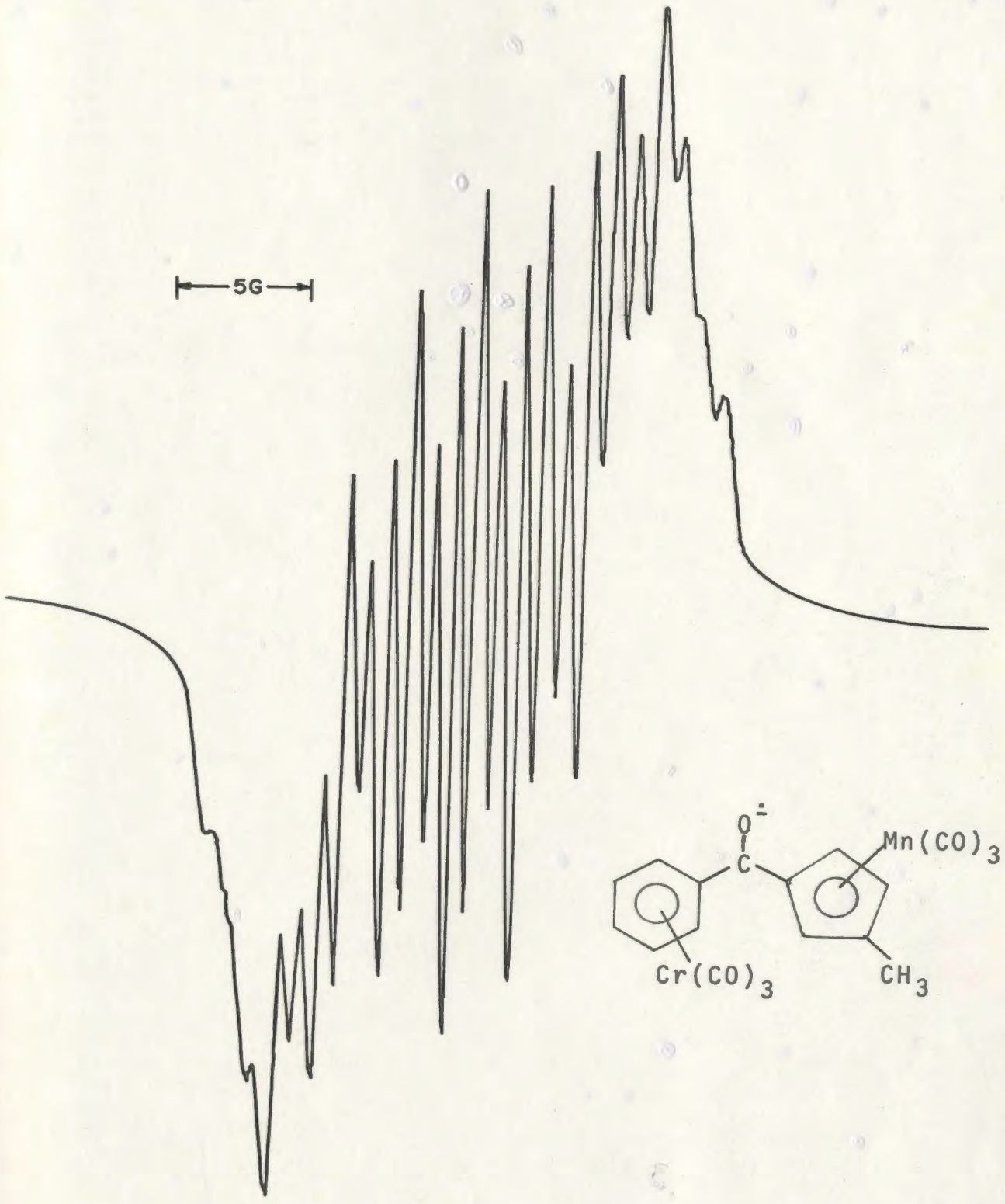
ESR Spectra Data of Some π-Radical Anions of the Type



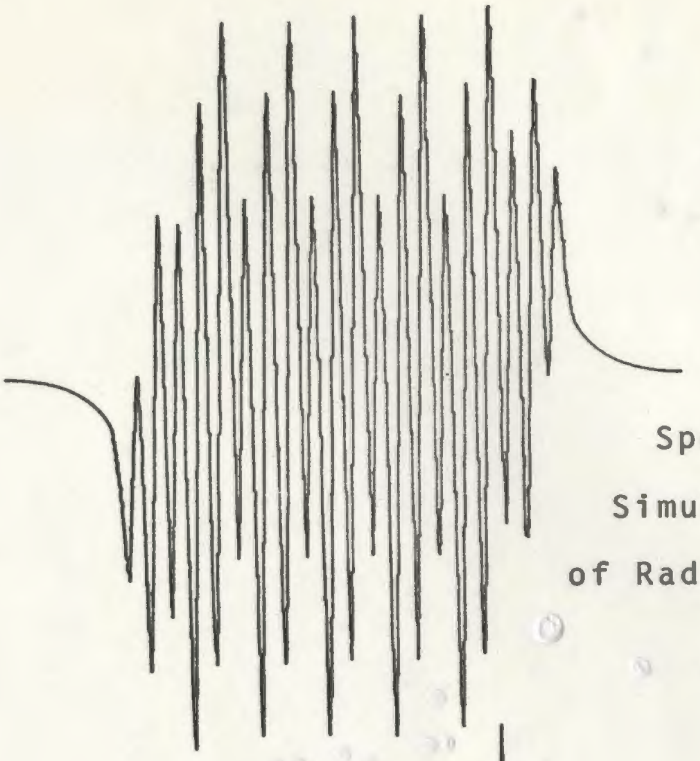
	Radical Anions		Hyperfine splitting constants (gauss)					
	R	R'	A_{Mn}	$A_{H(para)}$	$A_{H(ortho)}$	$A_{H(CH_3)}$	line-width	g
XVIII	H	H	2.41 ± 0.02	1.63 ± 0.01	0.80 ± 0.01	-	0.32	1.9998
XIX	H	α-CH_3	A Non-symmetrical Broad Band					2.0002
XX	H	β-CH_3	2.52 ± 0.03	1.61 ± 0.02	0.80 ± 0.02		0.22	2.0001
XXI	o-CH_3	H	5.11 ± 0.02			1.01 ± 0.01	0.80	1.9994
XXII	o-CH_3	α-CH_3	One Broad Band				18	2.0001
XXIII	o-CH_3	β-CH_3	5.20 ± 0.02			1.06 ± 0.01	0.82	1.9994
XXIV	m-CH_3	H	2.24 ± 0.03	1.53 ± 0.02	0.78 ± 0.02		0.51	1.9995

TABLE 6-3 (continued)

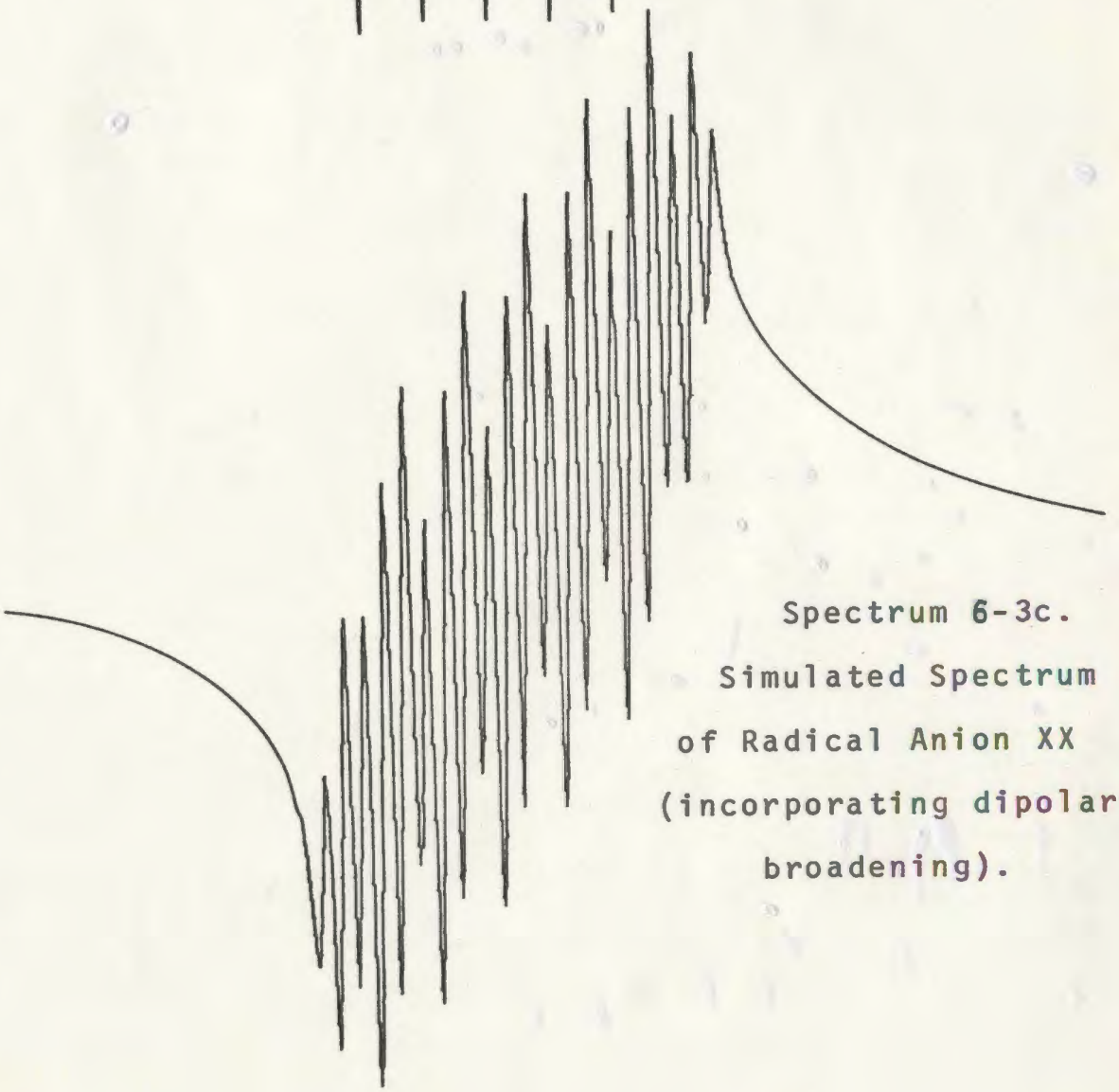
Radical Anions			Hyperfine splitting constants (gauss)					
	R	R'	A_{Mn}	$A_{H(para)}$	$A_{H(ortho)}$	$A_{H(CH_3)}$	line-width	g
XXV	m-CH_3	β-CH_3	2.51 ± 0.02	1.65 ± 0.02	0.83 ± 0.01		0.27	1.9995
XXVI	p-CH_3	H	3.05 ± 0.02			1.52 ± 0.01	0.48	1.9997
XXVII	p-CH_3	α-CH_3	1.62 ± 0.02			1.75 ± 0.01	1.50	1.9996
XXVIII	p-CH_3	β-CH_3	3.13 ± 0.03			1.54 ± 0.01	0.36	1.9994
XXIX	p-OCH_3	H	4.28 ± 0.04		1.35 ± 0.01		0.33	1.9989
XXX	p-OCH_3	α-CH_3	4.45 ± 0.03		2.70 ± 0.02		0.48	1.9982
XXXI	p-OCH_3	β-CH_3	4.40 ± 0.02		1.43 ± 0.02		0.38	1.9998



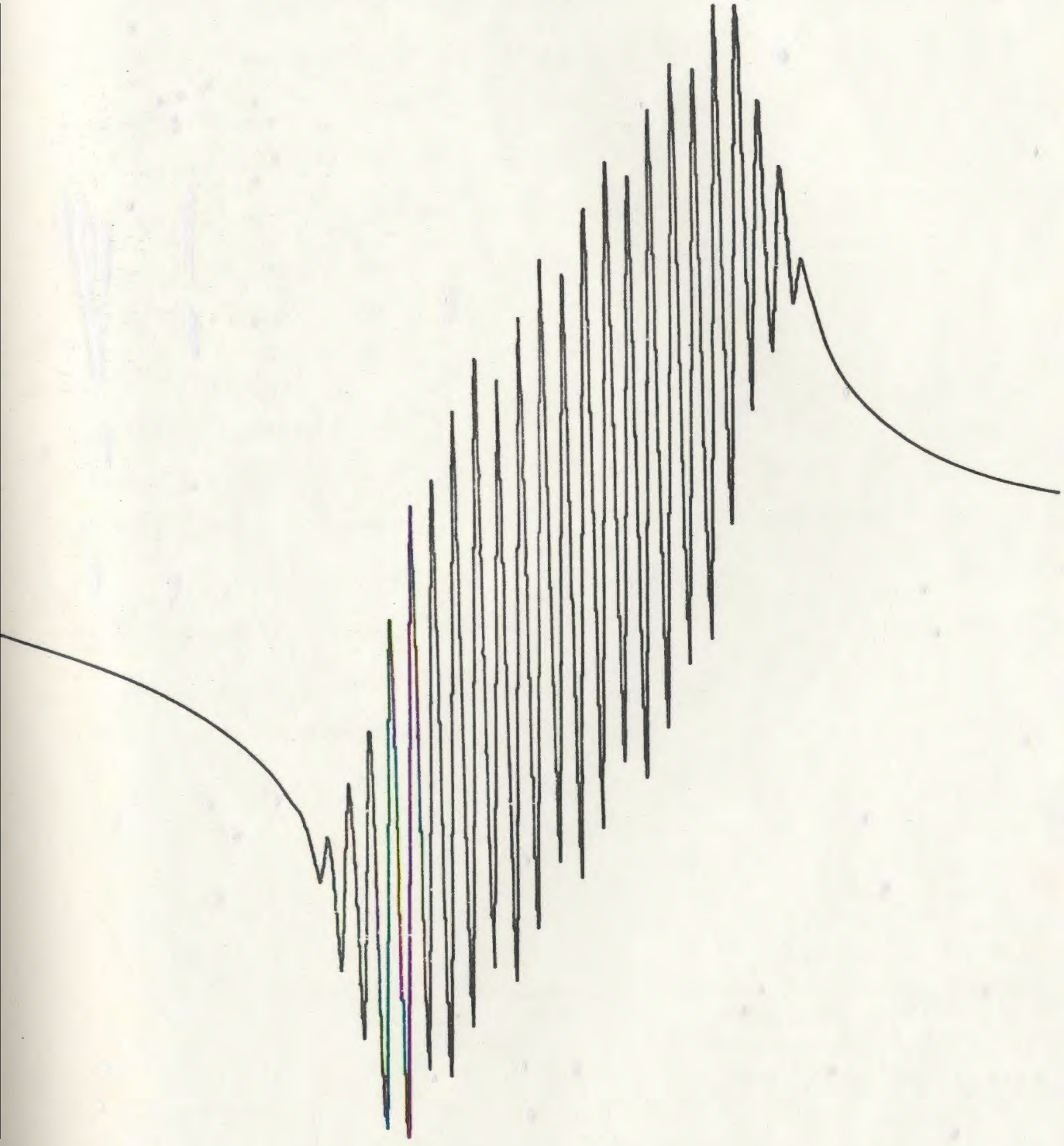
Spectrum 6-3a. ESR Spectrum of Radical Anion XX.



Spectrum 6-3b.
Simulated Spectrum
of Radical Anion XX.



Spectrum 6-3c.
Simulated Spectrum
of Radical Anion XX
(incorporating dipolar
broadening).

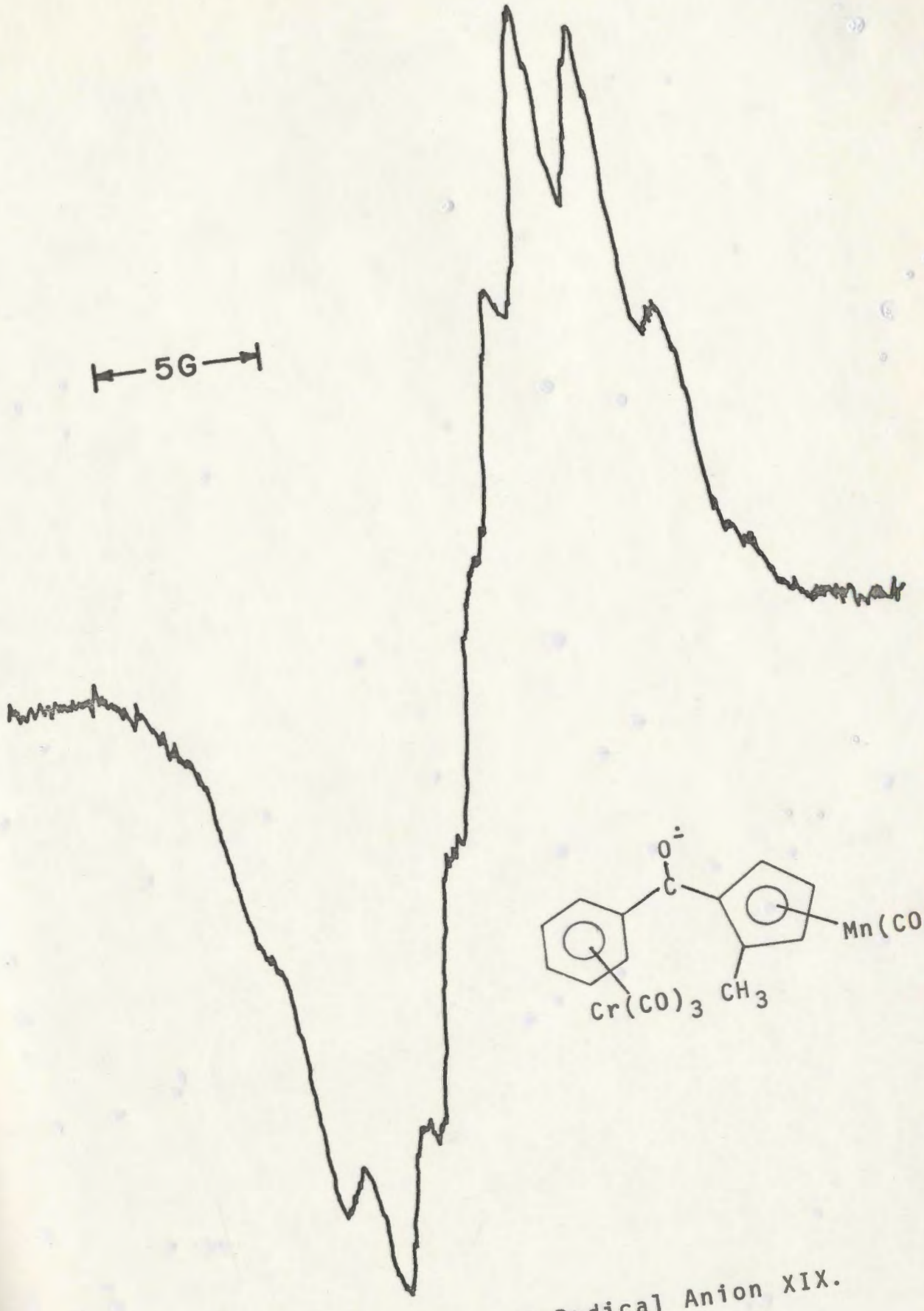


Spectrum 6-3d. Simulated Spectrum of Radical Anion XX (incorporating dipolar broadening and Cr^{53} satellites).

It is generally found that a methyl substituent at the meta position of the arene ring or at the β-position of the cyclopentadienyl ring does not change the splitting pattern of the unsubstituted radical anion. Only the splitting constants are slightly altered largely because the methyl group is electron donating. The spectra of radical anions XVIII, XXIV and XXV, for example, show splitting patterns similar to the spectrum of radical anion XX.

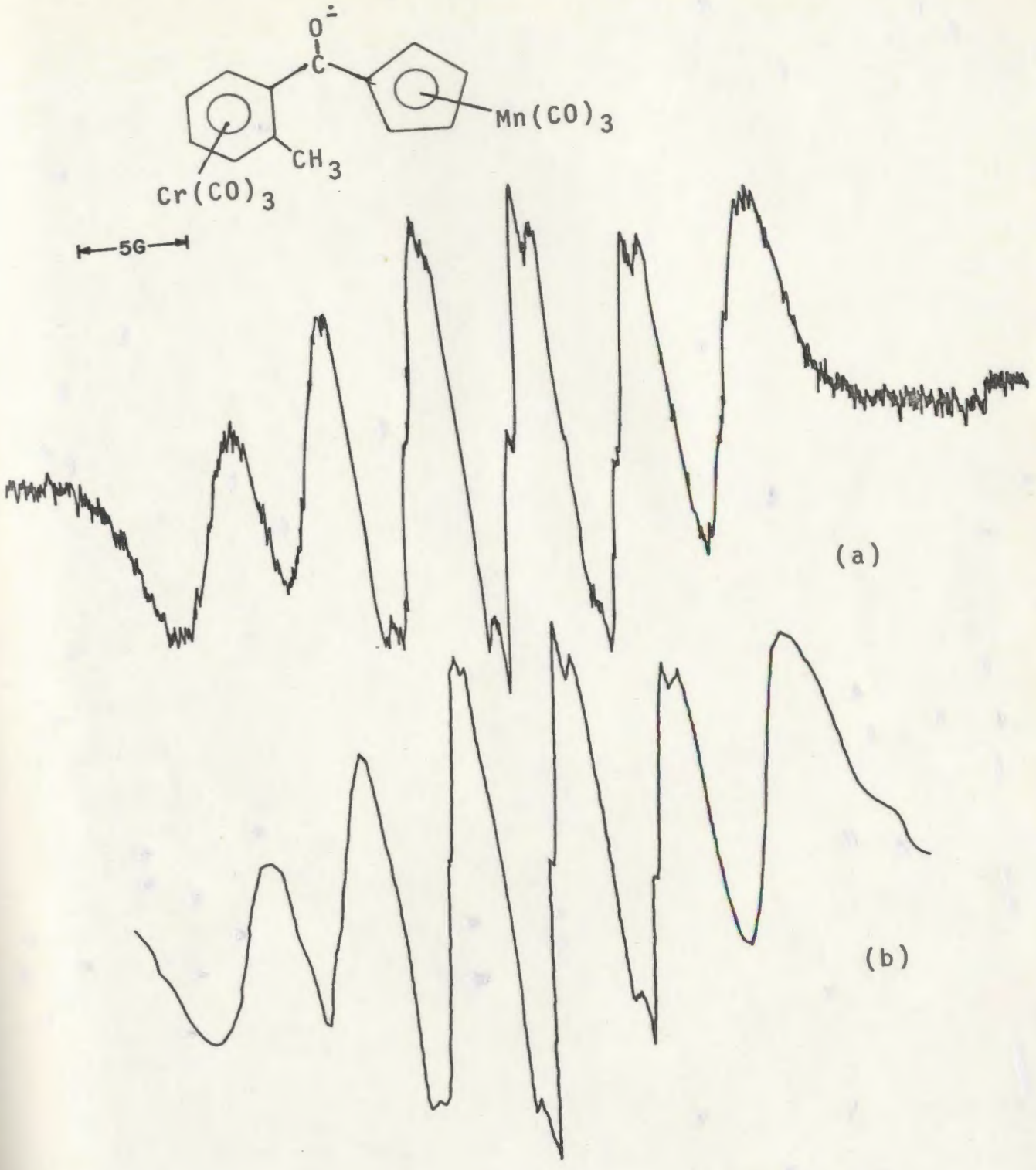
The spectrum of radical anion II shows a well defined splitting pattern whereas that of its $Cr(CO)_3$ complex, XIX, shows a non-symmetrical pattern (Spectrum 6-4). It appears from the spectrum of the latter that two paramagnetic species may be present. Fraenkel et al.[20] observed that radical anions of ortho substituted aromatic ketones do show rotational isomers. They suggested that these isomers have been formed by the 'locking-in' mechanism of the ketonic carbonyl with the aromatic ring. The NMR spectrum of the neutral ketone XIX does in fact suggest that the isomers are present. (Chapter 5).

The spectrum of radical anion XXI (Spectrum 6-5) has a very similar splitting pattern to that of radical anion XXIII. Six lines attributable to the Mn^{55} coupling are observed; each further splits into a quartet of relative intensities 1:3:3:1. This distribution precludes the



Spectrum 6-4. ESR Spectrum of Radical Anion XIX.

possibility that the splittings are due to the para and meta protons unless these three protons are magnetically equivalent. The simulated spectrum (Spectrum 6-5b) shows that the quartet is due to the coupling of the lone electron with the three equivalent methyl protons. Furthermore, the simulated spectrum also shows that the unresolved end lines are due to line broadening effects. The simulation has been carried out by varying the line-widths of the end lines until a good fit is obtained as shown. The A_{Mn} value (5.11G) is comparatively higher than that of $A_{H(CH_3)}$ (1.01G). Also the hyperfine splitting constants of the phenyl protons are so low that they are hardly observed at all. This is further confirmation that the ortho substituted methyl group is inhibiting delocalisation of spin density into the phenyl ring. In addition, the spectrum of radical anion XXII, in which the ortho position of the arene ring and the α-position of the cyclopentadienyl ring are both methyl substituted, shows only one broad band of line-width 18G but no hyperfine structure. Perhaps the spin density is now concentrated around the neighbouring atoms of the ketonic carbonyl and do not contribute to the observed hyperfine splittings. As a result, the splitting constants of the Mn^{55} atom and ring protons are considerably reduced causing the narrow hyperfine lines to coalesce into a single broad band. This is



Spectrum 6-5. ESR Spectrum of Radical Anion XXI. (With Simulation) (b)

supported by EHMO calculations[13] which show that the calculated spin densities agree very well with the experimental values. (Table 6-4).

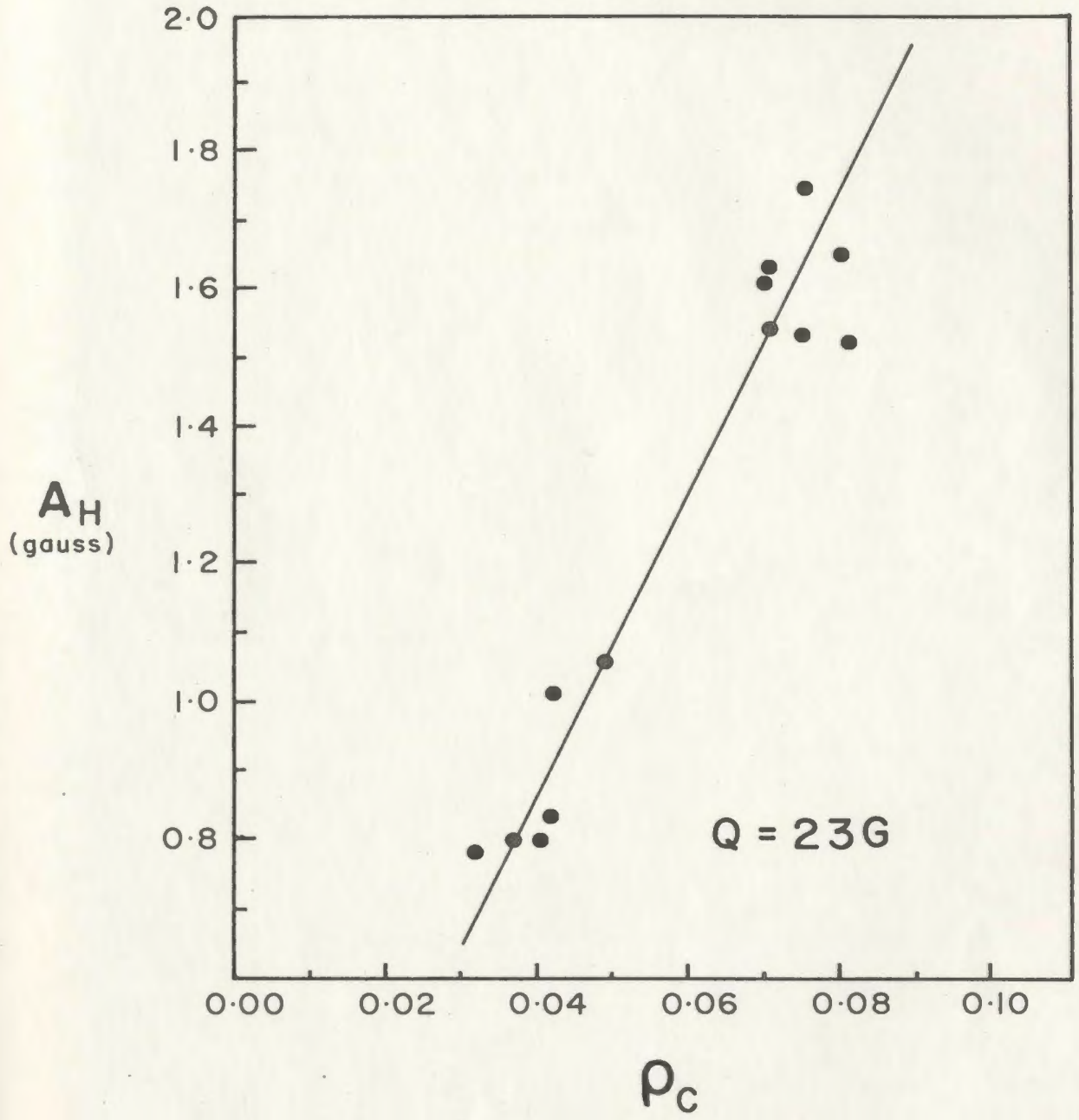
The experimental spin densities are obtained by using McConnell's equation,

$$\rho_C = A_H / Q$$

The value of Q is obtained from the best fit (Fig. 6-1 and Fig. 6-2) between observed hyperfine splitting constants and theoretical spin densities. It is noteworthy that the value of Q = -23G for the aromatic system is well within the calculated values of 20-30G suggested by McConnell[3].

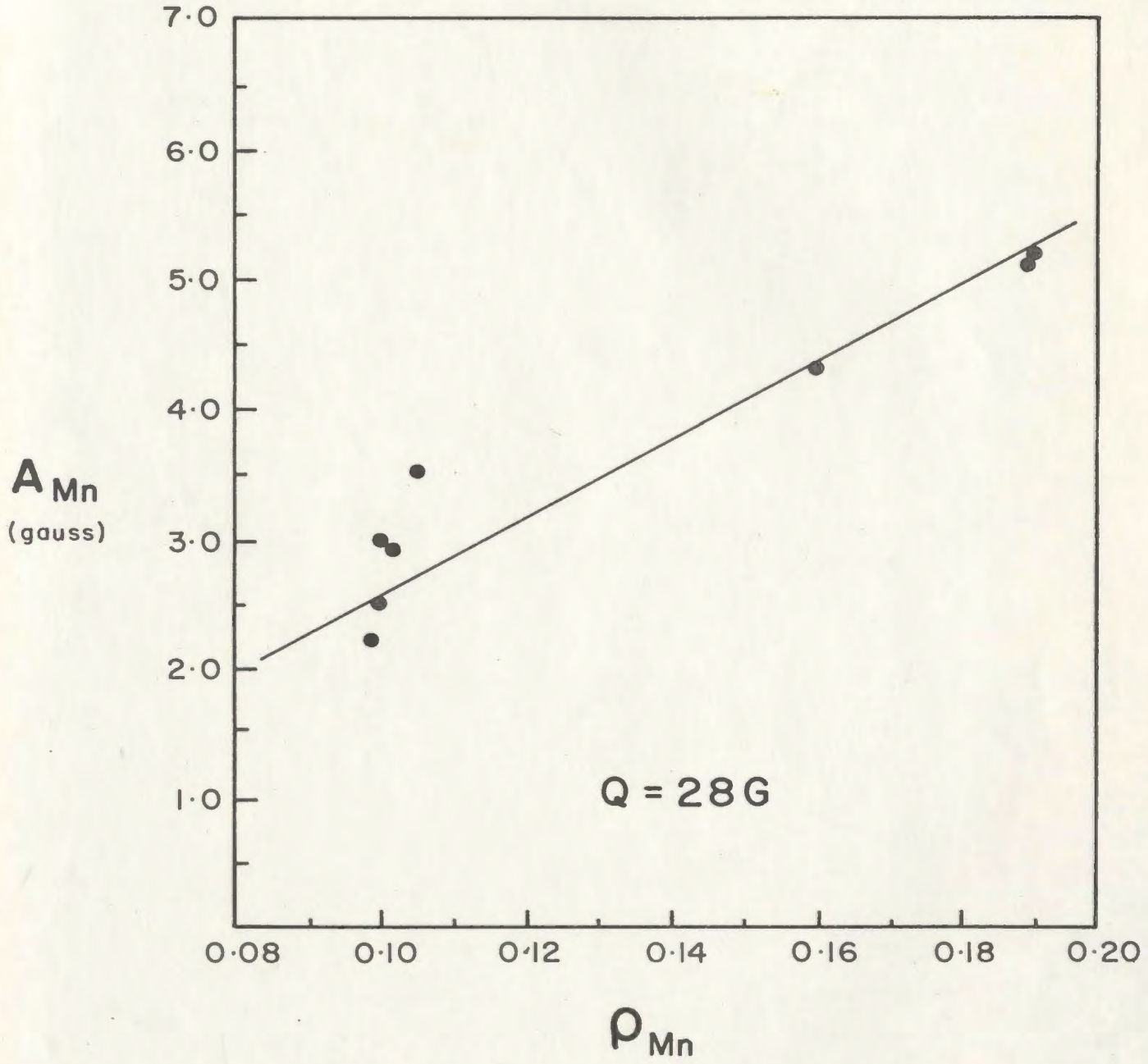
When the methyl group is substituted at the para position of the arene ring as in XXVI, and XXVIII, the lone electron of these radicals can become more delocalised into the arene ring. This is shown by the spectrum of radical anion XXVI (Spectrum 6-6). The higher value of the methyl proton hyperfine constant as compared to its ortho analogue indicates that a higher spin density is found on the para methyl protons than the ortho methyl protons. Correspondingly, the A_{Mn} value of radical anion XXVI is smaller than that of radical anion XXI. The simulated spectrum does not incorporate the Cr^{53} satellites, nor does it include dipolar broadening effects.

Fig. 6-1



Graph of observed proton hyperfine coupling constants (A_H) against calculated spin densities (ρ_c) at the ring carbon atoms for $\{[(CO)_3Cr]C_6H_4RCOC_5H_3R'Mn(CO)_3\}^{\cdot}$.

Fig. 6-2

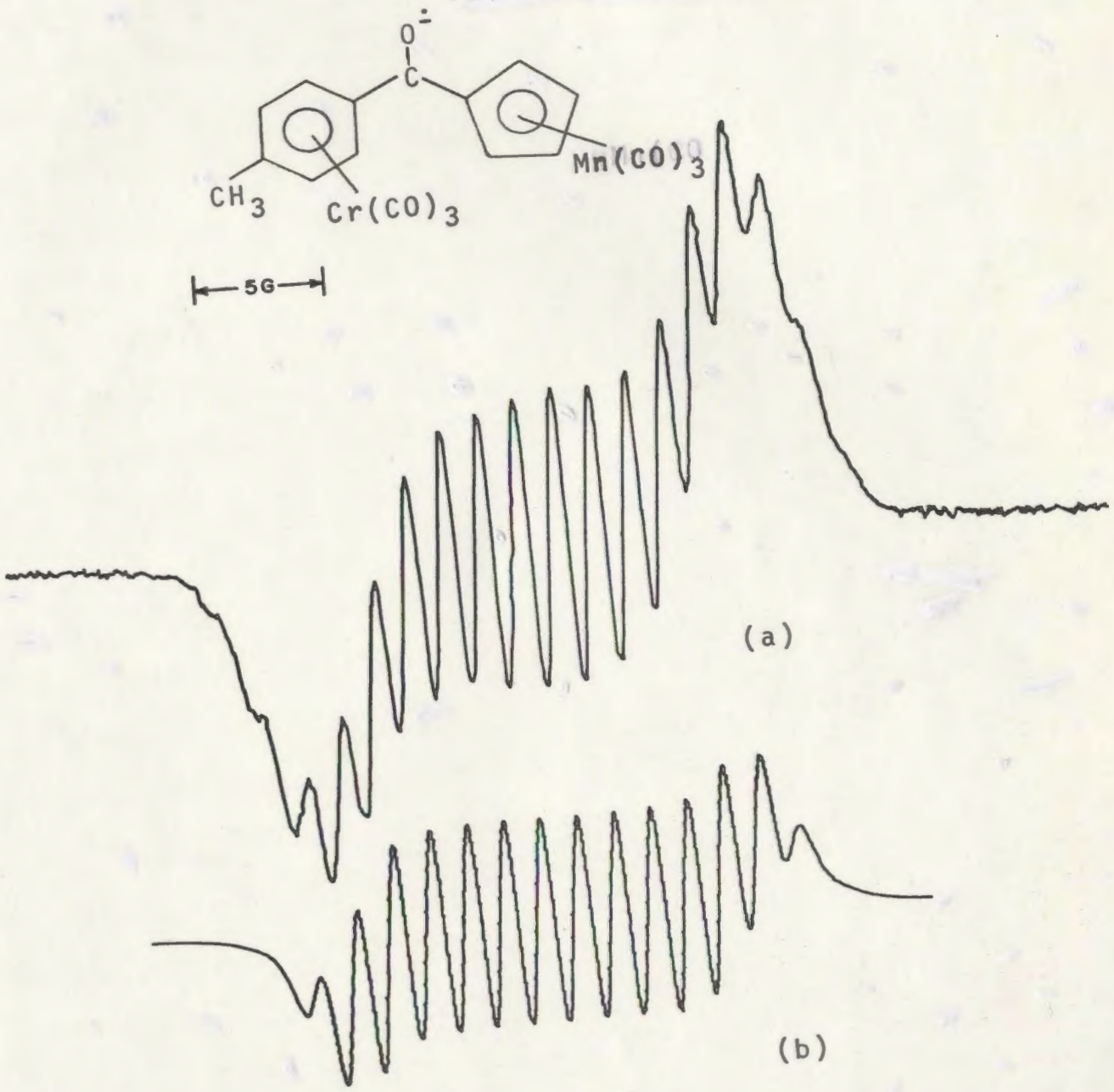


Graph of observed Mn^{55} splitting constants with calculated spin densities at the Mn nucleus for $\{[(CO)_3Cr]C_6H_4RCOC_5H_3R'Mn(CO)_3\}^{\cdot}$

TABLE 6-4

Experimental and Theoretical Spin Densities of $\{[(CO)_3Cr]C_6H_4RCOC_5H_3R'Mn(CO)_3\}^{\cdot-}$

		Experimental					Theoretical					
R	R'	ρ_{Mn}	ρ_c^p	ρ_c^o	ρ_c^m	$\rho_c^{CH_3}$	ρ_{Mn}	ρ_c^p	ρ_c^o	ρ_c^m	$\rho_c^{CH_3}$	ρ_{Cr}
H	H	0.086	0.071	0.035	<0.008		0.102	0.071	0.037	-0.008		0.103
H	β-CH_3	0.090	0.070	0.035	<0.008	<0.009	0.105	0.070	0.040	-0.009	0.008	0.104
o-CH_3	H	0.182	<0.007	<0.009	<0.008	0.044	0.189	0.011	0.017	-0.007	0.042	0.097
o-CH_3	α-CH_3	<0.042	<0.009	<0.008	<0.008	<0.009	0.092	0.011	0.013	-0.009	0.012	0.097
o-CH_3	β-CH_3	0.186	<0.007	<0.008	<0.008	0.046	0.190	0.012	0.015	-0.006	0.049	0.086
m-CH_3	H	0.080	0.066	0.034	<0.008	<0.009	0.099	0.075	0.032	-0.001	0.009	0.087
m-CH_3	β-CH_3	0.090	0.072	0.037	<0.008	<0.009	0.098	0.080	0.041	-0.001	0.007	0.072
p-CH_3	H	0.110	<0.006	<0.008	<0.008	0.066	0.100	0.012	0.012	-0.007	0.081	0.102
p-CH_3	α-CH_3	0.058	<0.006	<0.008	<0.008	0.076	0.051	0.012	0.012	-0.006	0.075	0.067
p-CH_3	β-CH_3	0.112	<0.006	<0.008	<0.008	0.067	0.112	0.009	0.021	-0.005	0.071	0.071

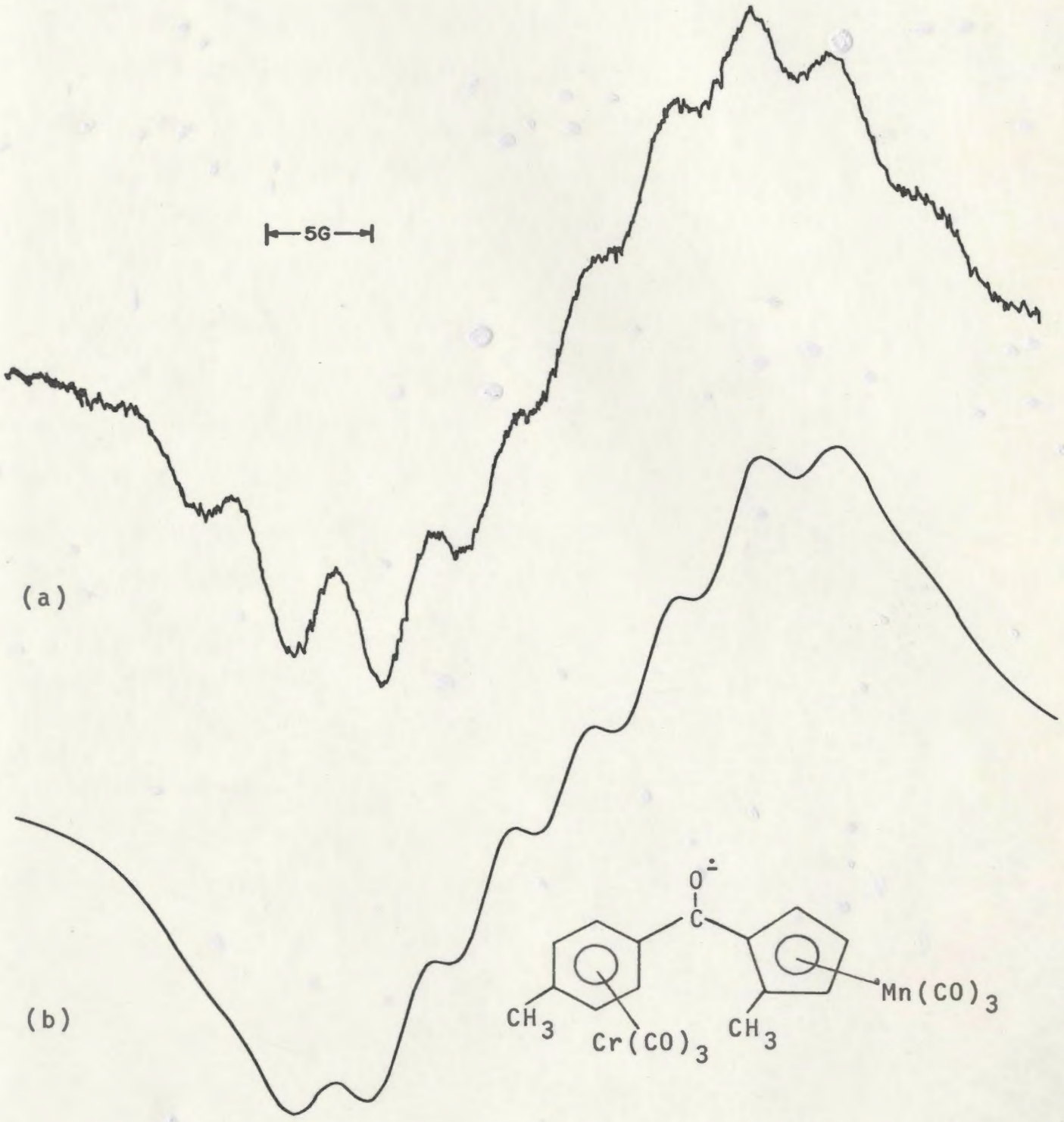


Spectrum 6-6. ESR Spectrum of Radical Anion XXVI. (With Simulation) (b)

However, a good fit having the correct relative intensities and splitting constants is obtained with the observed spectrum.

The strong electron withdrawing $Cr(CO)_3$ group on the arene ring reinforced by the electron repelling methyl group at the α-position of the cyclopentadienyl ring reduces the spin density on the manganese atom so much that it is difficult even to distinguish the six manganese hyperfine lines from the proton hyperfine lines. The radical anion XXVII is of this type and is shown in Spectrum 6-7. The simulated spectrum gives hyperfine constants as given in Table 6-3. Though it is not a perfect fit, it nevertheless gives the correct line positions and relative intensities in spite of the large line-widths and dipolar broadening effects.

The radical anions of anisole[21] are known to behave rather anomalously because of the ease of cleavage of the methoxy group by the alkali metal. Such a cleavage has not been observed in spectra of radical anions XXIX, XXX, and XXXI. Instead a normal one electron reduction seemed to have occured. The electron donating property of the para methoxy group is evident from the high value of the Mn^{55} splitting constant (4.28G) as compared with that of the corresponding para methyl analogue (3.05G). It does appear that electron donating groups on the arene ring

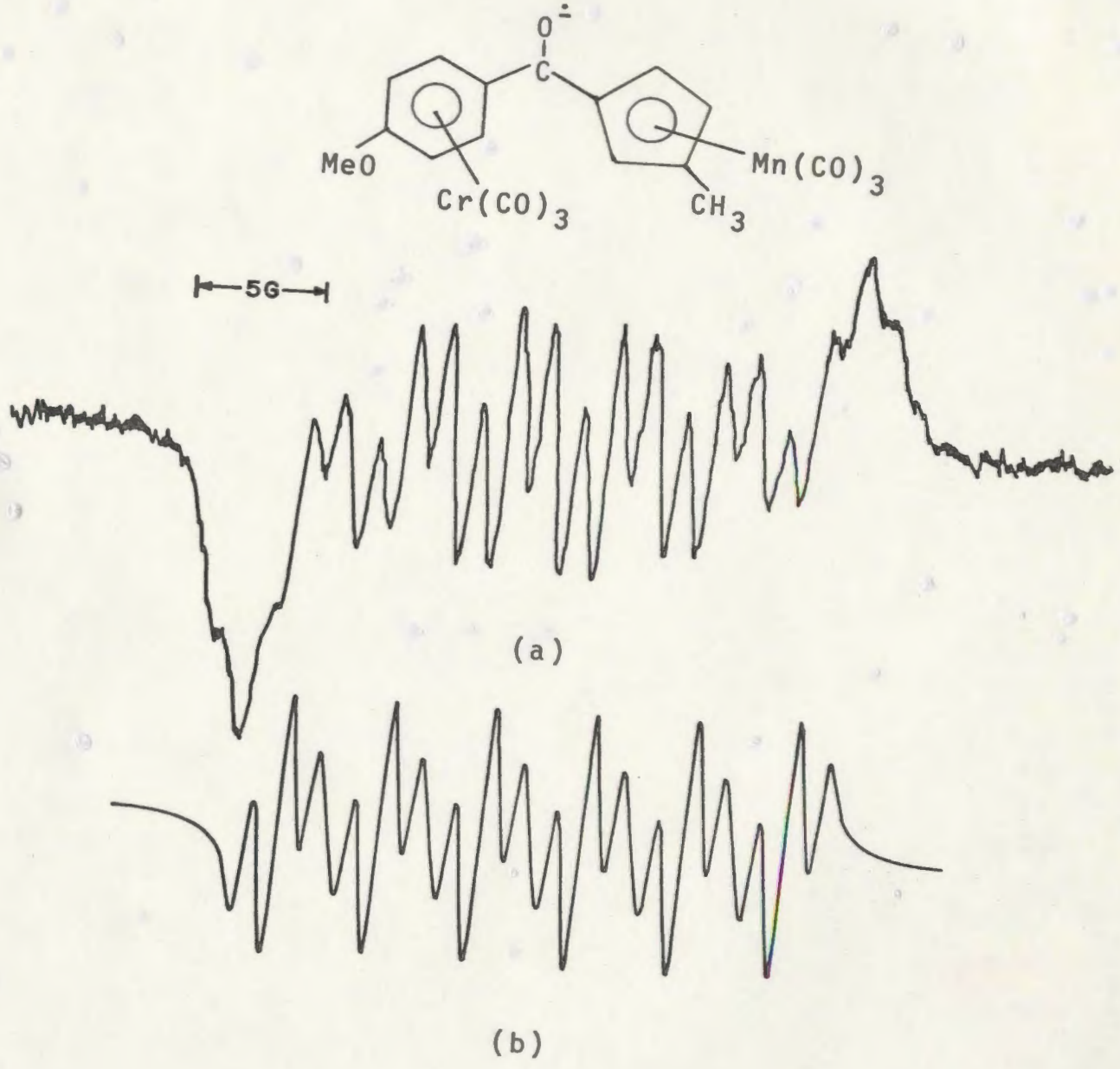


Spectrum 6-7. ESR Spectrum of Radical Anion XXVII. (With Simulation) (b)

inhibit spin delocalisation on the arene ring. No hyperfine structure attributable to the methoxy protons has been detected.

Unlike the para methyl substituted analogue, the radical anion of XXXI shows no hyperfine structure attributable to the methoxy protons (Spectrum 6-8). The lone electron appears to delocalise more onto the methyl protons than the methoxy protons. This is not surprising since the oxygen atom of the methoxy group is more electronegative than the corresponding carbon atom of the methyl group. However, a splitting constant of 1.43G which has not been observed in the methyl substituted analogue may now be attributed to the two ortho protons of the radical anion XXXI.

The spectrum of radical anion XXX in which a methyl group is substituted at the α-position of the cyclopentadienyl ring shows that the manganese splitting constant does not differ too much from those of radical anions XXIX and XXX. This is rather unexpected since the other radical anions show that a methyl substituent at the α-position of the cyclopentadienyl ring tends to reduce this value very significantly (Tables 6-1 and 6-3). Perhaps the p-methoxy substituent is such a strong electron donor that the α-substituent effect on the cyclopentadienyl ring is significantly offset. The high splitting constants of



Spectrum 6-8. ESR Spectrum of Radical Anion XXXI. (With Simulation) (b)

the ortho protons seem to support this view.

Generally, the A_{Mn} values of the radical anions in Table 6-3 seem to follow the same decreasing trend as those found in Table 6-1, viz. o-CH_3 > p-OCH_3 > p-CH_3 > m-CH_3 ∿ H.

EXPERIMENTAL

All the ESR spectra were obtained using a JEOLCO ME 3X ESR spectrometer operating at X-band. The magnetic field was measured with an NMR gaussmeter. The microwave frequency was measured by the beat method using a Micro-Now system. Both the microwave and NMR frequencies were measured with a TS1 385-R counter. The spectra were recorded at various temperatures for optimum resolution using a JES-VT3 model temperature control unit.

Simulation of spectra were obtained from the output of an IBM 370 and the magnetic tapes were then fed into a PDP-12 computer equipped with a CALCOMP plotter.

Purification of DME.

Analar grade DME (Ansul) was first dried over anhydrous $CaCl_2$. This was then refluxed over dispersed sodium for two hours in an inert atmosphere of N_2. It was then distilled and the flask containing the distillate was connected to a vacuum line previously flushed with N_2. The distillate was again distilled into another flask coated with potassium. This process was repeated until a deep blue coloration in the DME was obtained.

Preparation of Radical Anions.

The set-up for the generation of radical anions is

shown in Fig. 6-3. The vacuum line was carefully flushed with dry deoxygenated nitrogen. Approximately 10^{-4} mole of the ketone was introduced into the base of the reaction tube. A small grain (ca. 10 mg) of freshly cut potassium washed in dry ether was carefully placed into the side-arm of the reaction tube by means of a nickel wire. The system was then evacuated. The reaction tube was warmed with a hair-blower to remove any volatile impurities that might be adsorbed in the inner wall of the tube. The stop-cock was closed and the base of the tube was cooled in a flask of liquid nitrogen, so as to protect the sample from thermal decomposition during the heating. A piece of aluminium foil was placed between the flask and the side-arm of the tube to prevent direct heating of the flask. A potassium mirror was formed by carefully heating the potassium with a micro-burner. The non-volatile oxides were left on the side-arm. The tube was then allowed to cool. 1.5 ml of the highly purified DME measured out in a graduated tube connected to the vacuum line were then distilled under vacuum to the reaction tube now cooled in liquid nitrogen. The reaction tube was pumped on for a minute before the stop-cock was closed and the tube disconnected from the vacuum line. The reaction tube was shaken and at the same time allowed to warm up to room temperature.

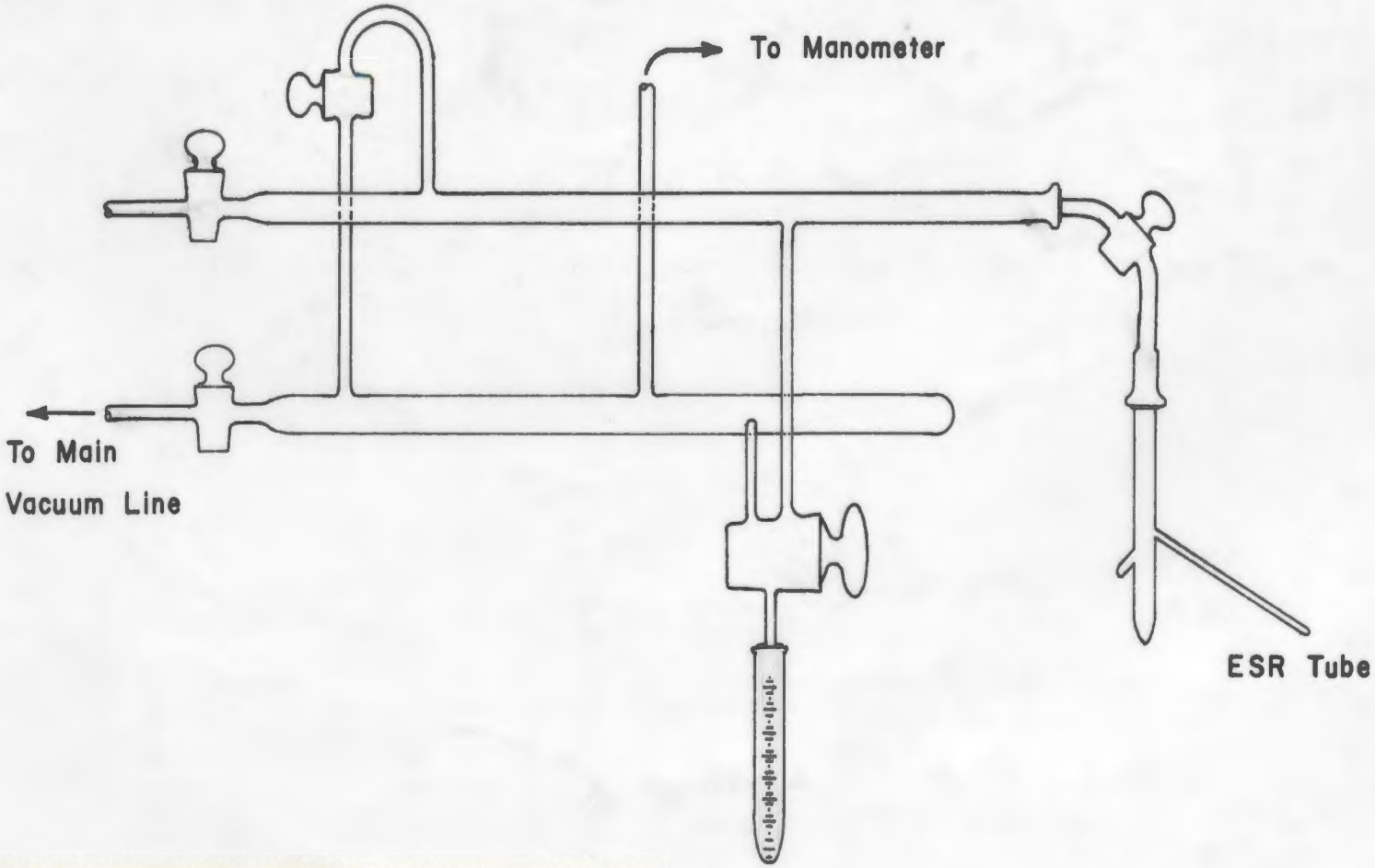


Fig. 6-3

Vacuum System For Preparing Radical Anions

Precautions were taken not to allow the impurities in the side-arm to mix with the solution. Dilution of the radical solution was carried out by immersing the ESR tube in a bath of liquid nitrogen and allowing the DME to distil over.

CONCLUSION

The ESR spectra of radical anions of $C_6H_5COC_5H_4Mn(CO)_3$ derivatives show hyperfine lines attributed to the manganese nucleus, and the para and ortho protons of the phenyl ring. No resolvable hyperfine lines have been observed for the meta protons of the phenyl ring and the cyclopentadienyl protons. This indirectly suggests that the electron density at these positions is high and are not favoured by the occupation of the free electron. The observation is consistent with the relative ease of electrophilic substitution reactions of the cyclopentadienyl ring as compared to the phenyl ring.

The fact that the para and ortho positions are more affected than the meta positions shows that the effect of the substituent is indeed conjugative and involves the π-orbitals of the system. This is further supported by the spectra of ortho methyl-substituted radical anions in which the loss of conjugation can be interpreted as a

steric effect of the methyl group resulting in a loss of coplanarity of the π-molecular orbitals in the system.

A large fraction of the spin density is drawn from the whole π-system when the $Cr(CO)_3$ group is complexed to the arene ring. Perhaps the spin density is now more localised on the Cr-ring bond.

It is concluded, therefore, that the metal orbitals of the $M(CO)_3$ moieties contribute significantly to the π-bonding of the metal-ring bond.

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CHAPTER 7
MASS SPECTROSCOPY

INTRODUCTION

The study of mass spectroscopy of organometallic compounds is comparatively new. One of the reasons, perhaps, is that the fragmentations of these compounds are often complicated by the catalysis of unwanted decompositions by the metal ions formed during the fragmentation[1]. The fragmentation patterns of even simple molecules are often too complicated to be explained without a certain amount of conjecture. Processes such as labelling studies[2], appearance potentials[3] and analysis of shapes and intensity ratios of metastable[4] bands have been attempted to elucidate the structures of such ions. The ionic structures appearing in the literature are often fictitious. They are however, necessary for visualising the various fragmentation paths.

GENERAL FRAGMENTATION STUDIES

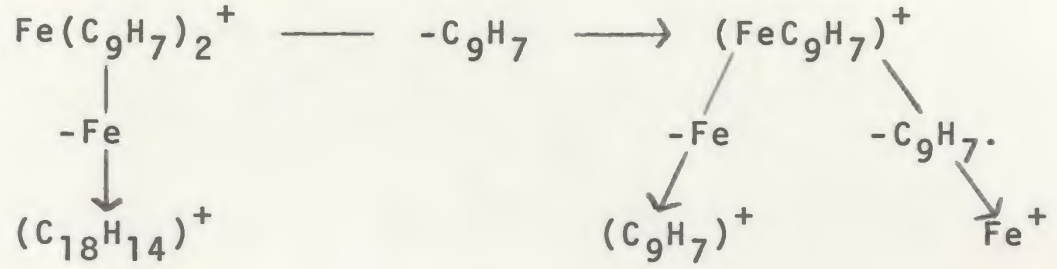
In organometallic complexes, the most vulnerable centre for excitation is the central metal atom where most of the positive charge resides[5]. The electron from the highest occupied molecular orbital, which is normally non-bonding or weakly bonding, is removed on ionisation.

Table 7-1 shows the ionisation potentials (I.P.) of some organometallic complexes[6]. Generally, the I.P. of these complexes are closer to those of the free metals than those of the free ligands.

TABLE 7-1[6]

Complex	I.P. (eV)	I.P. of free metal atom (eV)	I.P. of free ligand (eV)
$Cr(CO)_6$	8.20	6.76	14.01
$Cr(C_6H_6)_2$	5.91	6.76	9.25
$Cr(C_5H_5)_2$	6.26	6.76	8.69
$Fe(CO)_5$	8.14	7.87	14.01
$Fe(C_5H_5)_2$	7.15	7.87	8.69
$Ni(CO)_4$	8.64	7.63	14.01
$Ni(C_5H_5)_2$	7.16	7.63	8.69

The implication of these results is two-fold; the decomposition of a complexed ligand is usually different from that of the free ligand, and the positive charge usually remains on the fragment containing the metal. King[7], however, observed that, for condensed aromatic hydrocarbons, the charge often remains with the ring, for example, the fragmentation of bis(π-indenyl)iron.



The metal-ligand dissociation energies of compounds of the type ML_x^+ increase with loss of L. For example, Miller and his co-workers[8] observed that the appearance potentials for the ions P^+, $(P-CO)^+$, $(P-2CO)^+$, and $(P-3CO)^+$ in arene-chromium tricarbonyl were 6.74, 7.25, 8.09, and 10.34 eV, respectively. The intensities of the molecular ions are therefore generally very weak and at times completely unobserved. On the other hand, complexes having π-bonded aromatic ligands such as bis-π-benzenechromium[9] and ferrocene[10] do show strong molecular ion peaks. Unlike carbonyl complexes, the loss of the first ligand often requires more energy than loss of the second.

Müller[6] classified ligands into two main groups; the readily removed ligands such as CO, NO, N_2, H, PF_3, CH_3, PH_3, olefins, and the not so readily removed ligands like F, allyl, aromatic hydrocarbons and cyclic oligo-olefins. It is believed[8] that the electron removed during ionisation comes from an orbital derived mainly from a metal d-orbital involved in back-bonding with the ligand. Hence, on ionisation, the metal-ligand bond of strong electron--accepting ligands tends to be destabilised, whereas, that

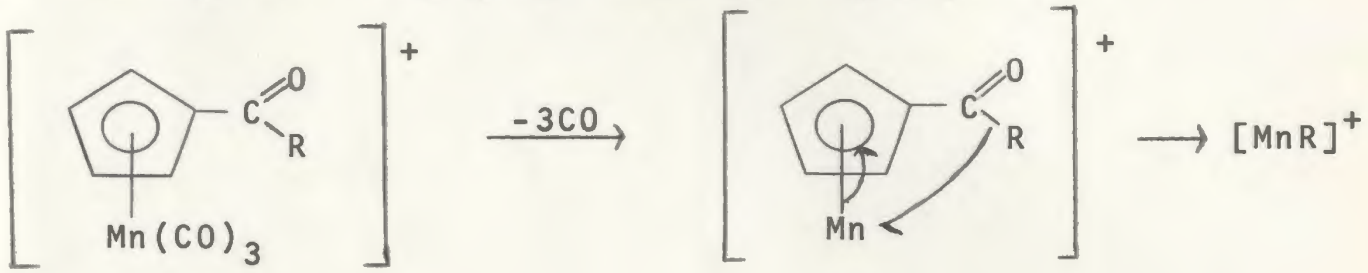
of electron-donating ligands is stabilised and not so readily removed.

FRAGMENTATION OF CYCLOPENTADIENYL COMPLEXES

The fragmentation pattern of $(C_5H_5)_2Mn$ resembles more of the ionic $(C_5H_5)_2Mg$ than those of covalent $(C_5H_5)_2M$ where M = V, Cr, Fe, Co and Ni[11,12]. This suggests that the bonding between the ring and manganese atom is mainly ionic. It has been estimated that the metal-ring bond strength for manganese is substantially less than that for other first-row transition metals. Winters and Kiser[13] observed that the Mn-CO bond is weaker than the Mn-ring bond in $C_5H_5Mn(CO)_3$. The carbonyls are removed in two steps; the first involves the simultaneous removal of two CO molecules followed by the loss of the third CO molecule. The relative abundances observed are P^+ (25.7%), $(P-CO)^+$ (0.2%), $(P-2CO)^+$ (22.7%), and $(P-3CO)^+$ (100%). The only $M(CO)_x^+$ species observed is MCO^+ (0.2%), and no cleavage of C-O bond has been observed. Fragmentation of the C_5H_5 ring in half-sandwich compounds of vanadium and cobalt gives $(C_3H_3M)^+$, $(C_3H_2M)^+$, and $(C_2HM)^+$ but these are often observed in very low abundance.

An interesting feature in the fragmentation process of $RC_5H_4Mn(CO)_3$ is the ability of the substituent R to

migrate from the ring to the metal. Cais and co-workers[14] suggested that such a migration takes place only with α-substituted carbonyl derivatives ($RCOC_5H_4Mn(CO)_3$ where R = H, CH_3, OH, $(CH_2)_nCO_2H$ and $CH_2COCO_2C_2H_5$, e.g.



When the side-chain R contains two or more carbons, bi-cyclic structures are believed to be formed.

FRAGMENTATION OF ARENECHROMIUM DERIVATIVES

Pignataro and Lossing[15] and other workers[9,16] found that bis-π-benzenechromium decomposes to give ions corresponding to $[(C_6H_6)_2Cr]^+$, $(C_6H_6Cr)^+$, $(C_6H_6)^+$ and Cr^+. Very low abundances of the ions $(C_4H_4Cr)^+$, $(C_3H_3Cr)^+$ due to fragmentation of the benzene ring are observed.

The mass spectra of mixed π-complexes $(C_5H_5)M(C_6H_6)$ where M = Mn or Cr indicate preferential elimination of the C_6H_6 ring[9]. The abundance of $(C_6H_6Mn)^+$ ion is low but the corresponding hydride $(C_6H_6MnH)^+$ is four times as abundant.

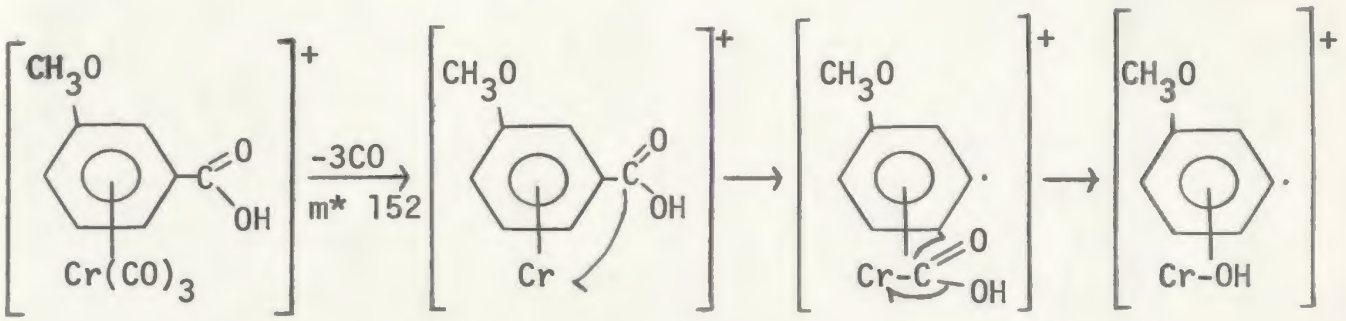
$$(C_5H_5MC_6H_6)^+ \longrightarrow (C_5H_5M)^+ + (C_6H_6M)^+ \longrightarrow M^+$$

It has been suggested that the stability of the C_5H_5-M

bond is greater than that of C_6H_6-M.

Half-sandwich π-arene metal carbonyl complexes of the type $RC_6H_5M(CO)_3$ have been studied by several workers[17,18]. Bursey et al.[19] found that $C_6H_6Cr(CO)_3$ exhibits very intense peaks corresponding to the ions $[C_6H_6Cr(CO)_3]^+$, $(C_6H_6Cr)^+$, and Cr^+ while those of $[C_6H_6Cr(CO)_n]^+$ (n = 1, 2) are found to be relatively weak. Fragmentation of the ring is not significant and no thermal decomposition is evident at temperatures below 300°.

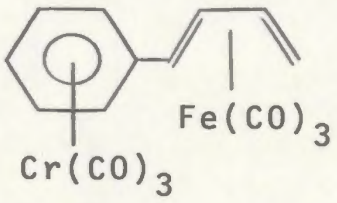
Rearrangement processes have also been proposed for the fragmentation of α-ketonic derivatives of (anisole) chromium tricarbonyl, for example,

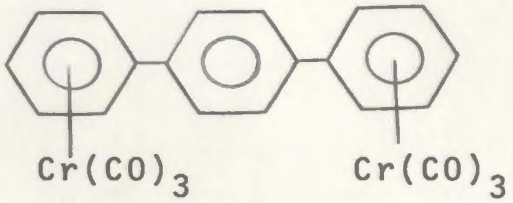


A metastable transition corresponding to the loss of four carbonyl groups from the molecular ion has been observed. It is believed that this process is a one-step mechanism in which the carboxylic group migrates to the Cr atom. This is followed by the loss of the ketonic CO.

The mass spectra of some bimetallic complexes have

also been studied[21], e.g.

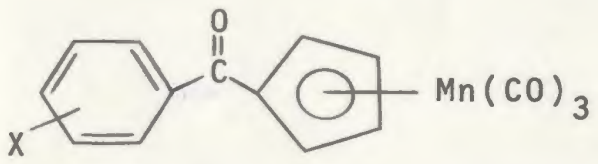




Bimetallic ions $(Cr\text{-}Cr)^+$ and $(Cr\text{-}Fe)^+$ have been observed. The elimination of carbon monoxide molecules is not readily predictable but it does not appear to occur in a stepwise manner. It is suggested that the loss of three CO molecules in one step followed by a stepwise loss of the remaining three CO molecules cannot be ruled out.

RESULTS AND DISCUSSION

The mass spectra of several $RC_5H_4Mn(CO)_3$ derivatives have been previously studied. Fragmentation involving the substituent R often complicates the analysis of these spectra. Since both the cyclopentadienyl and arene rings are known to be relatively stable to fragmentation the mass spectra of systems of the type



X = H, CH_3, OCH_3, Cl, F

will be of interest.

The present study also includes double metal-carbonyl complexes in which the arene ring of the above derivatives is complexed with a $Cr(CO)_3$ group. It is hoped that the spectra of these complexes will enable a general fragmentation pattern to be deduced and perhaps yield some information of their relative metal-ligand bond strengths. The spectra of some non-conjugated systems will also be discussed.

The spectra were recorded on a Hitachi-Perkin-Elmer RMU-6E Spectrometer using a direct inlet system. The percentage abundance quoted in this study is taken relative to the most intense peak (the base peak).

GENERAL FRAGMENTATION PATTERN

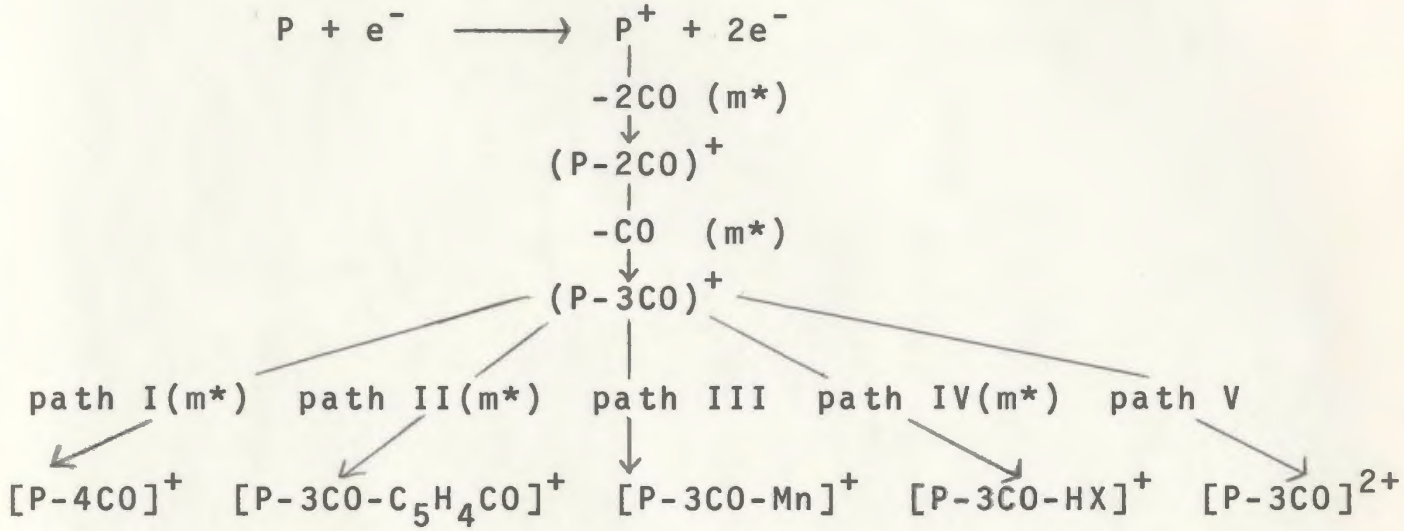
$C_5H_5Mn(CO)_3$ derivatives are generally more stable than metal-carbonyls like $M(CO)_n$. As such their parent ions are found to be more abundant and often as high as 25% of the base peak. The $(P + 1)^+$ peak has an abundance corresponding to that calculated for the presence of a single ^{13}C. No ion-molecule reaction is suspected since no peaks having m/e value higher than $(P + 1)^+$ are observed.

The loss of CO molecules is not a stepwise process. Instead it appears that two CO molecules are simultaneously removed initially, followed by the loss of the third CO molecule to give the ion $(P-3CO)^+$ which in most of the spectra studied is the base peak. Metastable bands for these two processes are observed in all the spectra and the relative abundance of the ion $(P-CO)^+$ is very low ($\sim$ 0.1%). No fragmentation of the ring is observed until all the carbonyls are removed. Neither is there any evidence of C-O cleavage.

Further fragmentation of $(P-3CO)^+$ can follow several competitive paths (Fig. 7-1); the loss of the ketonic CO molecule group (Path I), decomposition to form more stable ions like $(ring + M)^+$ (Path II), loss of neutral metal atom (Path III), loss of the substituent X (Path IV), and formation of a doubly charged ion (Path V).

Fig. 7-1

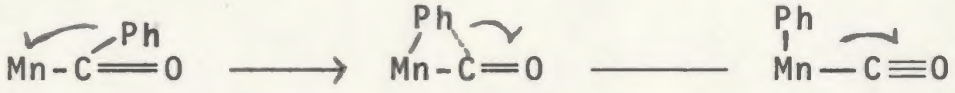
Initial Decomposition Paths of $XC_6H_4COC_5H_4Mn(CO)_3$



m* = observed metastable

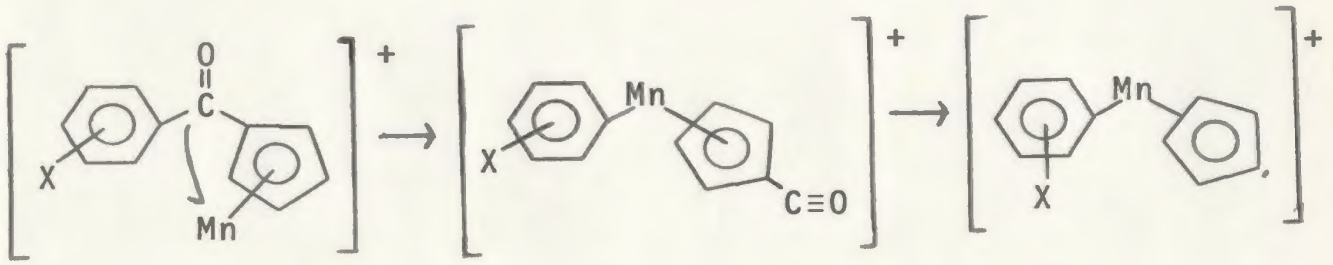
Path I

The loss of the ketonic CO group is probably an intramolecular rearrangement analogous to the decarbonylation mechanism[22,23] of the type



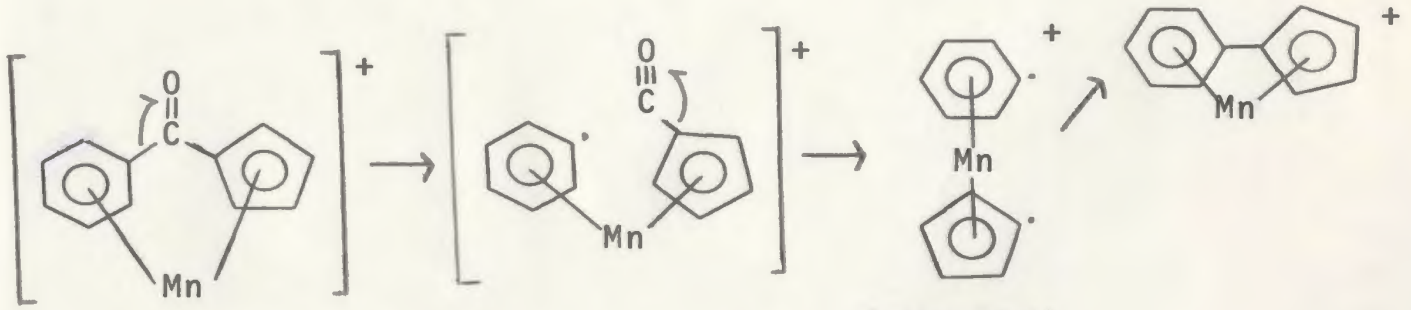
where the phenyl ring first forms a 'partial bond' with the metal to be followed by the removal of the CO molecule. This is perhaps not a suitable analogy but it does show that the ketonic CO is capable of being removed without disrupting the whole molecule. Furthermore, it is known

that the phenyl group is a good migrating group under mass spectroscopic conditions[21]. It is therefore possible that this step involves the migration of the arene group to the metal followed by the removal of the CO molecule. (Mechanism 1a).



Mechanism 1a

It is also possible that this mechanism is facilitated by the participation of the manganese atom (now devoid of the three carbonyl groups) with the π-orbitals of the arene ring. (Mechanism 1b).



$[P-3CO]^+$ (m/e 196)

Mechanism 1b

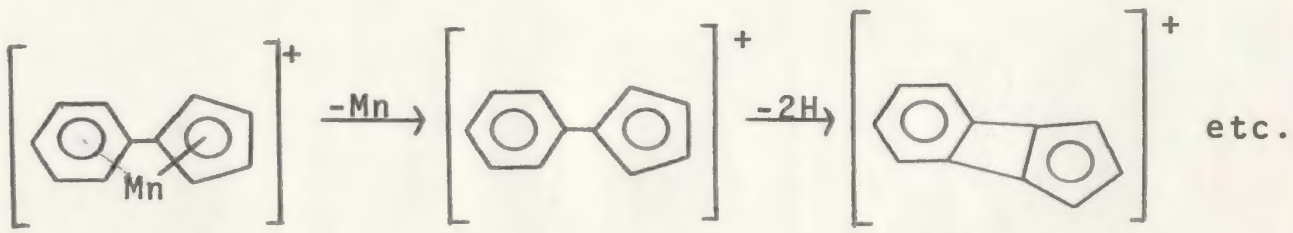
There are reasons to believe that the structure of $(P-3CO)^+$ is as shown in the figure and will be discussed later in

the chapter.

The possibility that the loss of the ketonic CO by the cleavage of two ring-CO bonds and then recombining is rather remote.

$$[C_6H_5COC_5H_4Mn]^+ \xrightarrow{-CO} [C_6H_5\text{-}C_5H_4Mn]^+$$

This is illustrated by the spectrum of $C_6H_5C_5H_4Mn(CO)_3$ in which the ion $[C_6H_5\text{-}C_5H_4Mn]^+$ is found to be the most abundant. No ion attributable to that of $[C_6H_5Mn]^+$ is observed. This implies that the migration of the phenyl ring in such systems is not important and a different fragmentation path appears to be more suitable. The fragmentation may be explained by the figure below in which the loss of two hydrogen atoms is interpreted as a ring fusion process.

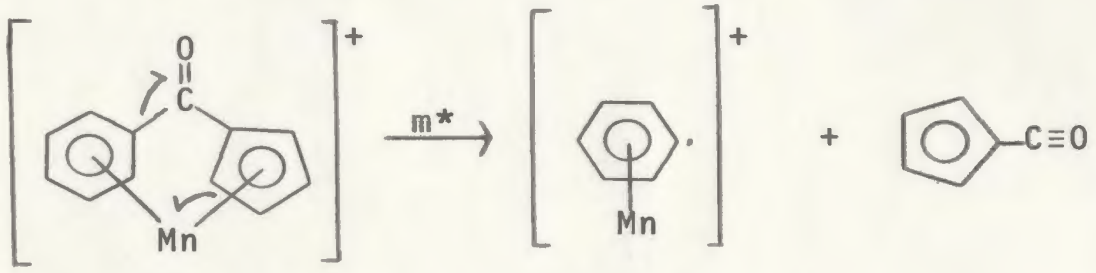


(m/e 196, 33%) (m/e 141, 100%) (m/e 139, 11%)

This fragmentation pattern has not been observed for the ketones. Therefore, it is unlikely that the loss of the ketonic CO involves the intermediate $[C_6H_5\text{-}C_5H_4Mn]^+$ ion.

Path II

It is difficult to explain the loss of the C_5H_4CO moiety from $(P-3CO)^+$ without introducing some form of intermediate ionic structure in which the manganese atom migrates intramolecularly. If the structure of $(P-3CO)^+$ as proposed in Mechanism 1b is assumed then the fragmentation may be as shown below.



(m/e 196) (m/e 132)

Path III

This path is not important in the fragmentation of ketones and only very low abundance of $[P-3CO-Mn]^+$ has been observed (< 3%). However, this loss of neutral metal becomes an important feature for systems like $C_6H_5C_5H_4Mn(CO)_3$ and $C_6H_5CH_2C_5H_4Mn(CO)_3$ which will be discussed in a later section.

Path IV

Generally, only the ortho substituted phenol and halo-benzene derivatives readily undergo this decomposition

step. The hydroxy and halogen are removed in the form of their hydrides. Meta and para substituted halides, on the other hand, are poor leaving groups and only very low abundances of $[P-3CO-HX]^+$ have been observed in such systems. The same is true for para substituted methyl and methoxy groups; in fact the methyl group is never a good leaving group, even when it is ortho substituted. Presumably it is stabilised by the formation of a tropylium type structure.

Path V

This process probably involves the second ionisation of the manganese atom. This doubly charged fragment $[P-3CO]^{2+}$ is observed in all the spectra studied and is most prominent in complexes where the substituents are electron withdrawing groups such as halides and hydroxy. Ions such as $[P-3CO+H]^{2+}$ and $[P-2CO+H]^{2+}$ have also been observed though in lower abundance (ca. 1%).

It is likely that these ions result from an ion-molecule reaction. Probably the $[P-3CO]^{2+}$ is first formed and subsequent reaction with a neutral species gives $[P-3CO+H]^{2+}$. This is preferred to an ion-ion interaction of the type $[P-3CO]^+ + H^+ \longrightarrow [P-3CO+H]^{2+}$ where the repulsion is expected to be high.

Fragmentation of Benzoylcyclopentadienylmanganese tricarbonyl.

Spectrum 7-1 is a normalised spectrum of $C_6D_5COC_5H_4Mn(CO)_3$. The fragmentation is similar to that of the non-deuterated analogue and a comparison between the two spectra helps to identify some of the fragments. Most of the fragments observed are identified and Fig. 7-2 is the proposed decomposition pattern.

The smaller fragments may be formed directly from any of the larger fragments and there is no reason to believe that they have been formed stepwise. In the non-deuterated complex, the observed peak at m/e 80 may be assigned to $(C_2HMn)^+$. It can be readily shown that the hydrocarbon part comes mainly from the cyclopentadienyl ring since no peak at m/e 81 attributable to the ion $(C_2DMn)^+$, has been observed in the spectrum of the deuterated analogue. The same can be said for the ion $(C_3H_2Mn)^+$. In general, it is observed that the cyclopentadienyl ring is more readily broken down than the phenyl ring under the conditions considered here.

Fragmentation Pattern of Some Methyl-substituted Benzoylcyclopentadienylmanganese Tricarbonyl Derivatives.

The most important difference between the fragmentation of methyl-substituted benzoylcyclopentadienylmanganese

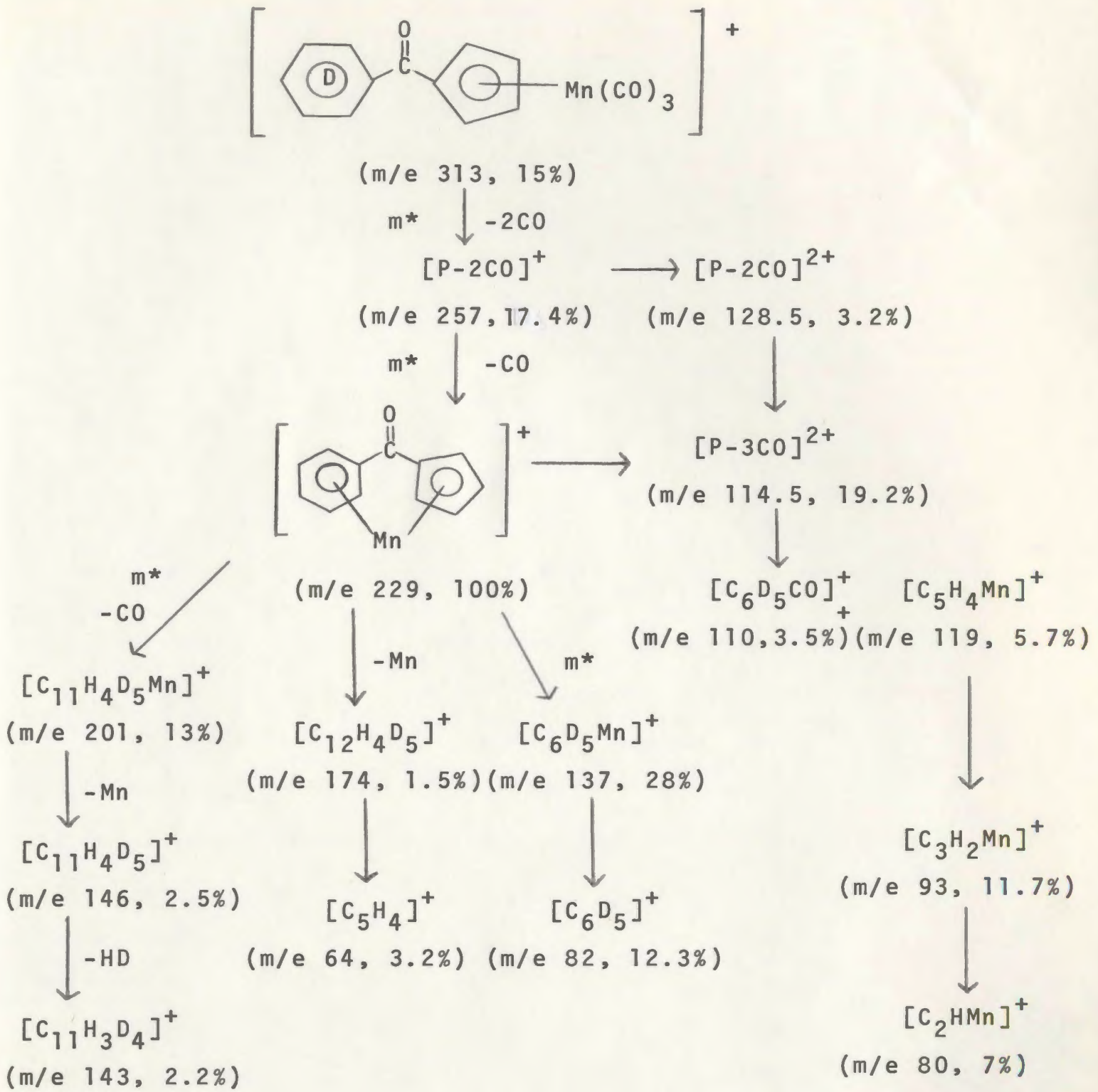
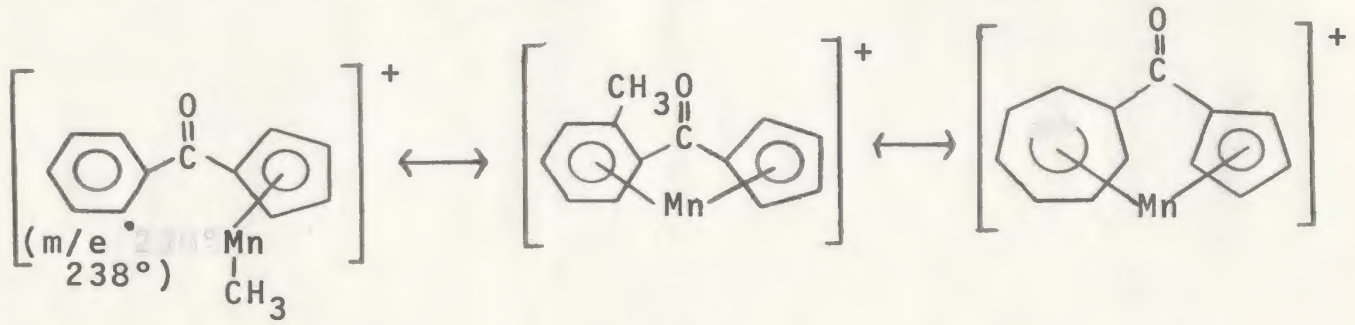


Fig. 7-2

Fragmentation Scheme of $C_6D_5COC_5H_4Mn(CO)_3$

tricarbonyl derivatives and those of the non-substituted analogues is probably the ability of the former to ring expand. No loss of methyl group has been observed in these complexes and the fragmentation patterns are surprisingly simple. The mass spectrum of o-$CH_3C_6H_4CO$-$C_5H_4Mn(CO)_3$ shows that the loss of CO molecules is again a two-step process (Fig. 7-3). The base peak at m/e 238 corresponds to the ion $(P-3CO)^+$. This ion can take one of several ionic structures e.g.



(a) (b) (c)

The tropylium ion $(C_7H_7)^+$ has been observed in all the spectra of toluyl derivatives studies. This, together with the fact that the ion $(C_6H_4)^+$ has not been observed in these spectra suggest that the structure (a) is unlikely. Furthermore, the fragmentation pattern of these toluyl complexes is very similar to that of $C_6H_5CH_2COC_5H_4Mn(CO)_3$ where the loss of a methyl group is not envisaged. However, it is difficult to distinguish between structure (b) and structure (c) without labelling studies.

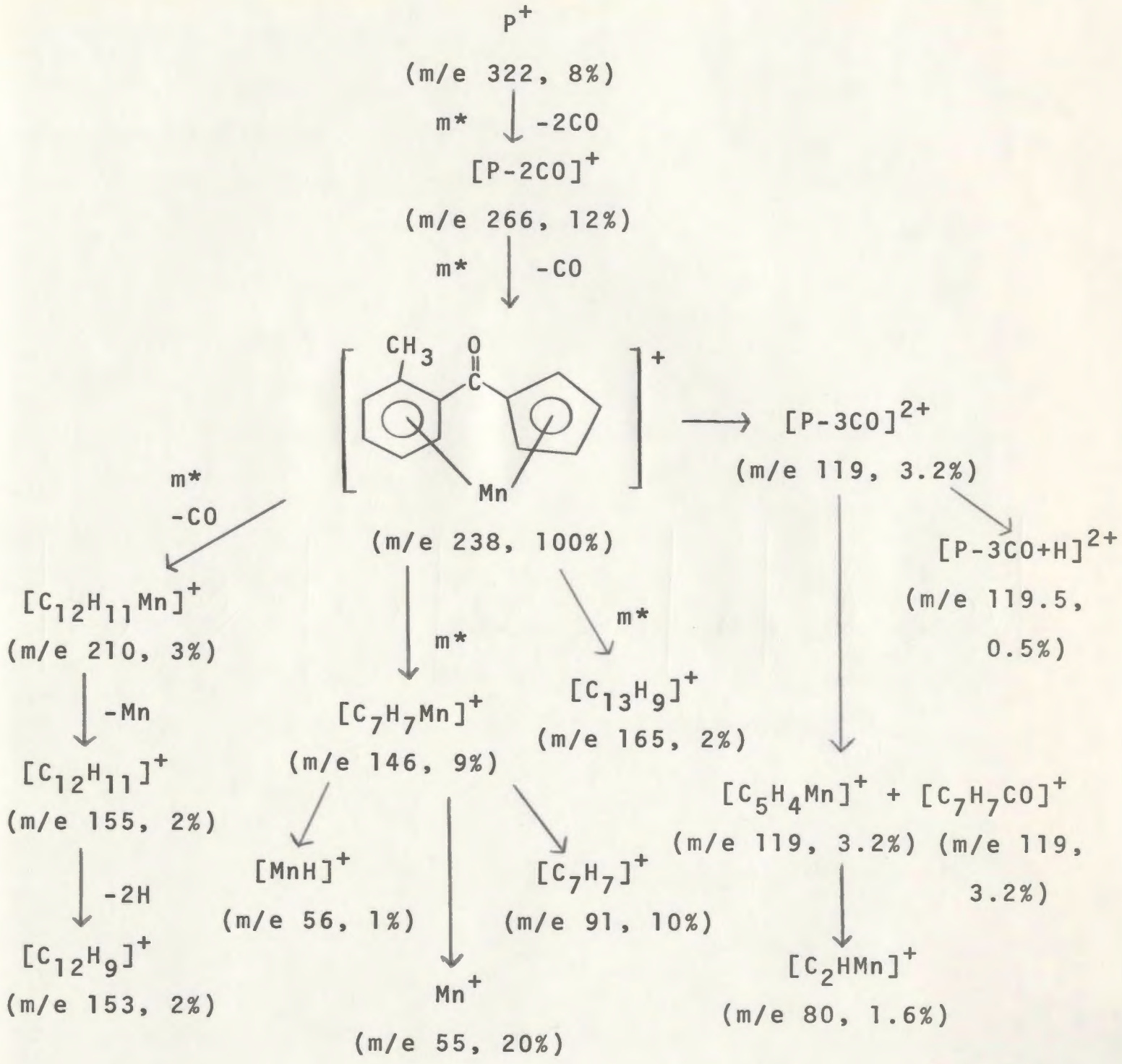


Fig. 7-3

Fragmentation Scheme of o-$CH_3C_6H_4COC_5H_4Mn(CO)_3$

The ion $[P-3CO]^+$ can decompose by several paths. The loss of the ketonic CO gives $(C_{12}H_{11}Mn)^+$ which then loses neutral manganese. This is followed by the loss of two hydrogen atoms, probably a ring closure process, to give $(C_{12}H_9)^+$ (m/e 153) (Fig. 7-3).

The formation of $(C_7H_7Mn)^+$ has been confirmed by a metastable transition. Presumably, this is more of a π-complex than a σ-complex which on decomposition gives $(C_7H_7)^+$. A metastable has been observed which corresponds to the formation of an ion having m/e 165. It is tentatively assigned to the ion $(C_{13}H_9)^+$.

An interesting feature observed in this spectrum is the presence of a doubly charged ion attributed to $(P-3CO)^{2+}$ (m/e 119). The decomposition of this ion is probably analogous to the decomposition of the doubly charged ion observed by Müller and Göser[16]

$$(C_5H_5MC_6H_6)^{2+} \xrightarrow{m^*} (C_5H_5M)^+ + (C_6H_6)^+ \quad (M = Cr \text{ or } Mn)$$

$$(C_5H_5MnC_6H_6)^{2+} \xrightarrow{m^*} (C_5H_5)^+ + (MnC_6H_6)^+$$

Correspondingly, the $(P-3CO)^{2+}$ (m/e 119) observed here can decompose to give $(C_5H_4Mn)^+$ (m/e 119) and $(C_7H_7CO)^+$ (m/e 119). That the peak at m/e 119 is due to all these three ions is shown by the spectra of other analogous derivatives.

In complexes where the methyl substituent is on the

cyclopentadienyl ring instead of the phenyl ring, the decomposition becomes a little more complicated (Fig. 7-4). This may be attributed to the increased fragmentation of the cyclopentadienyl ring. A comparative fragmentation study of $C_6H_5COC_5H_3(\alpha\text{-}CH_3)Mn(CO)_3$ and $C_6D_5COC_5H_3(\alpha\text{-}CH_3)$-$Mn(CO)_3$ (Spectrum 7-2) shows that the $(C_6H_5Mn)^+$ ion (m/e 132) observed in the former spectrum has not been observed in the latter spectrum. Instead a peak corresponding to $(C_6D_5Mn)^+$ (m/e 137) is observed. This implies that the $(C_6H_5Mn)^+$ ion has its hydrocarbon part from the phenyl ring and not from the cyclopentadienyl ring. Ions $(C_6H_5)^+$ (m/e 77) and $(C_6H_6)^+$ (m/e 78) have been shown in a similar fashion, to have their origin from the cyclopentadienyl ring.

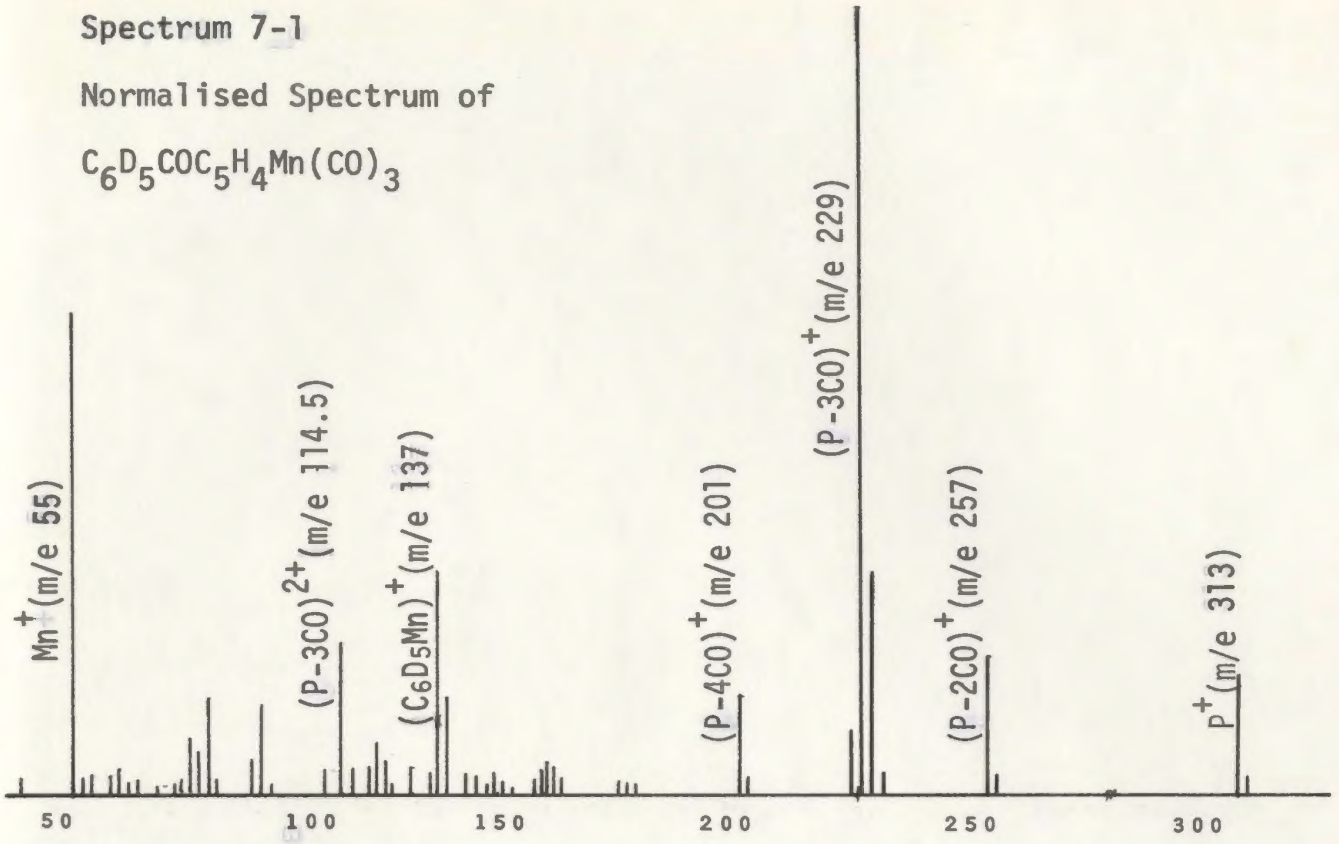
Fragmentation Pattern of Some Derivatives of $X\text{-}C_6H_4COC_5H_4$-$Mn(CO)_3$.

The initial fragmentations of complexes where X = Cl, F, OH, and OCH_3 follow the pattern previously discussed. It has been generally observed that para and meta substituents are poor leaving groups and very low abundance of ions corresponding to $(MnX)^+$ have been observed (ca. 0.5%). On the other hand, ions like $(XC_6H_4Mn)^+$ are often observed in much higher abundance (ca. 40%). It does appear that migration of substituent X is less important than the migration of the whole arene entity. It is possible that

Spectrum 7-1

Normalised Spectrum of

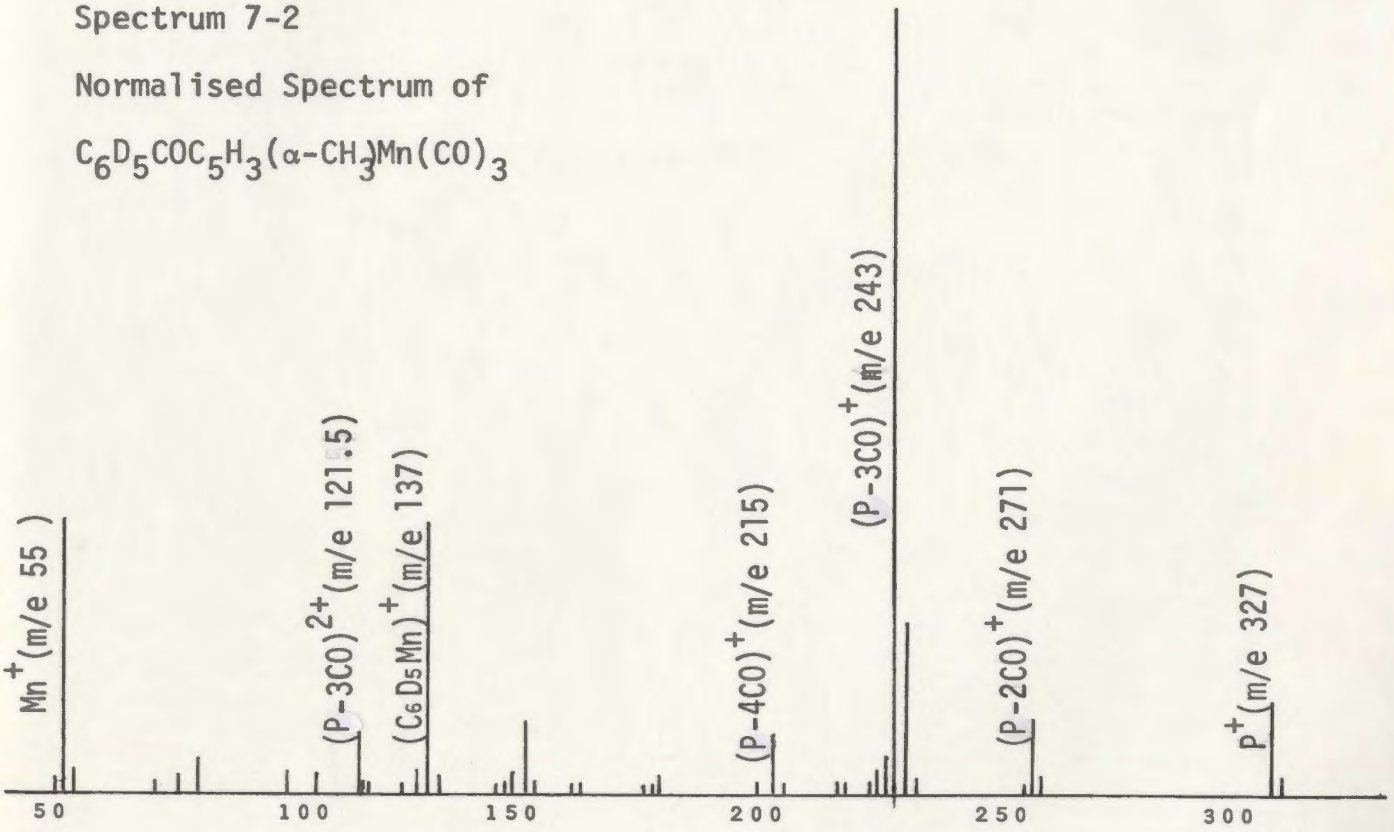
$C_6D_5COC_5H_4Mn(CO)_3$



Spectrum 7-2

Normalised Spectrum of

$C_6D_5COC_5H_3(\alpha\text{-}CH_3)Mn(CO)_3$



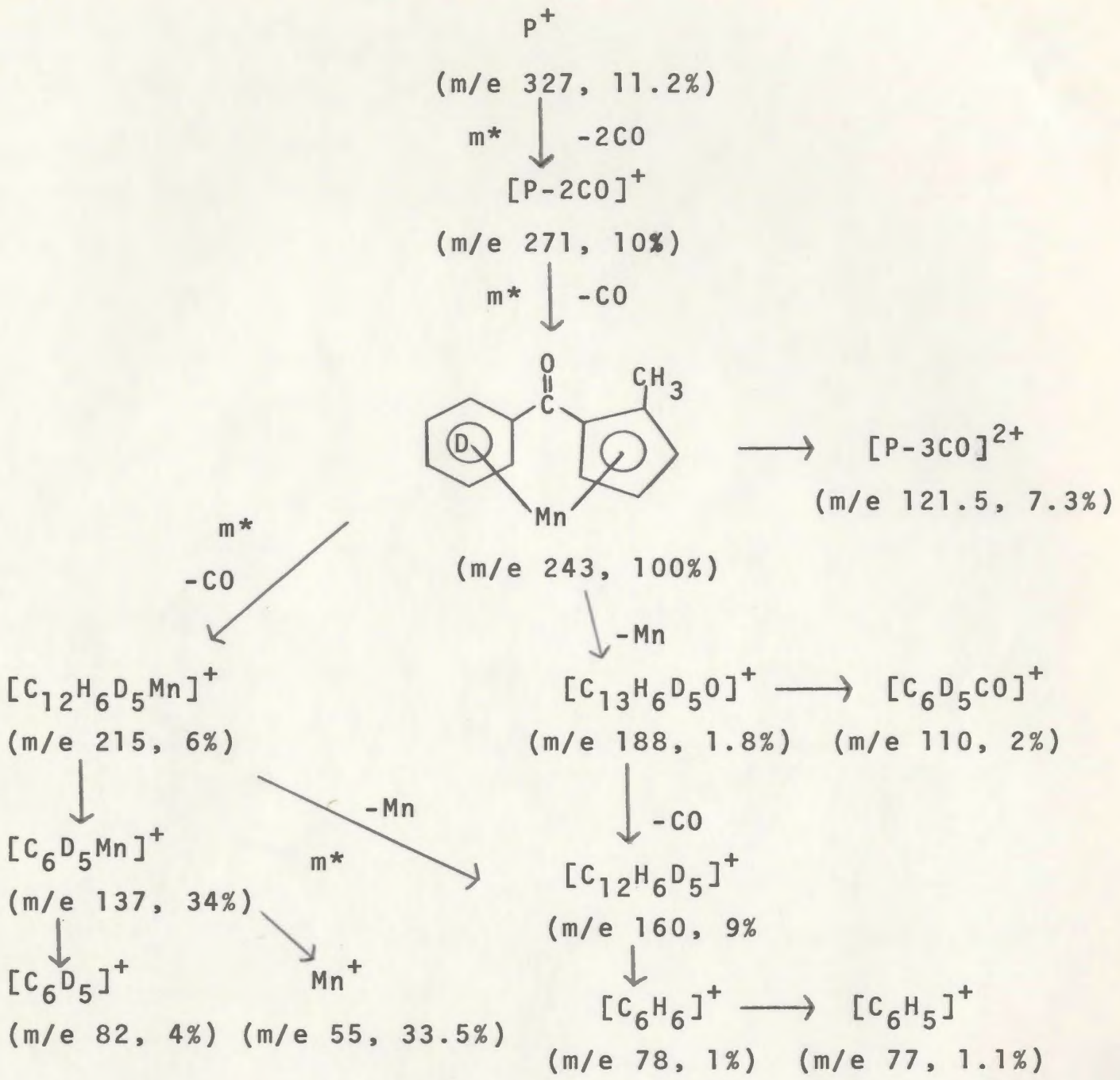


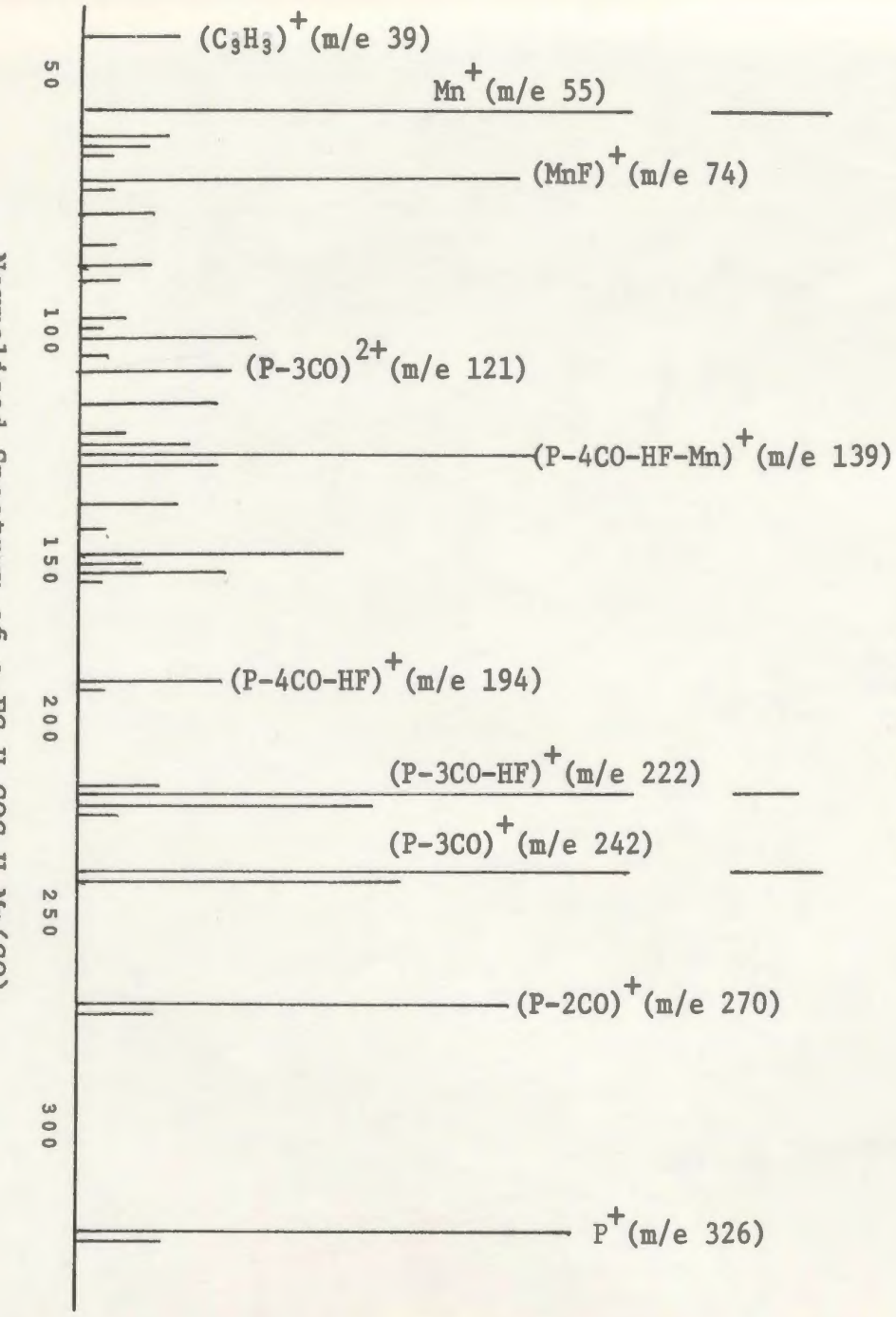
Fig. 7-4

Fragmentation Scheme of $C_6D_5COC_5H_3(CH_3)Mn(CO)_3$

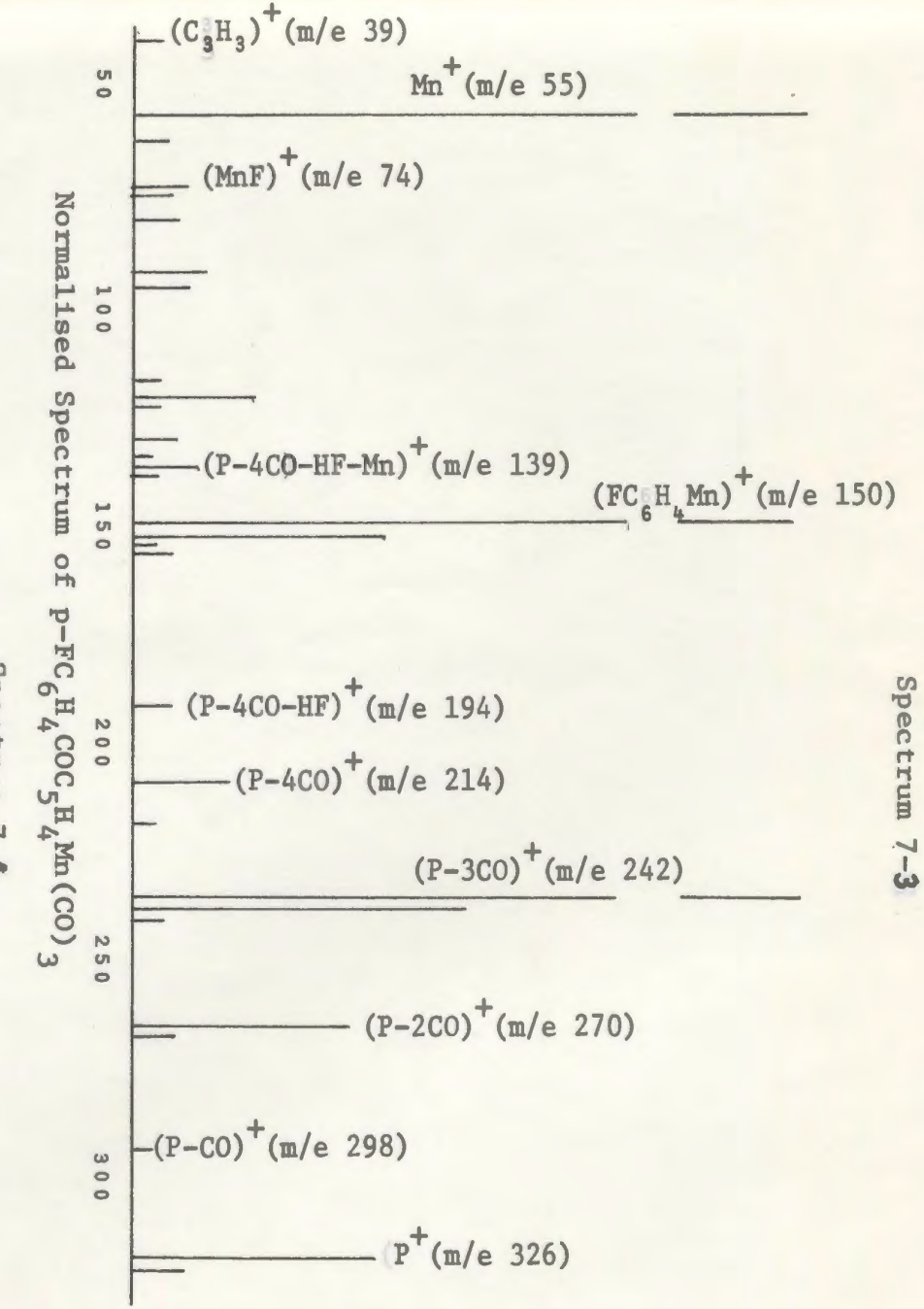
this $(X\text{-}C_6H_4Mn)^+$ ion further decomposes to form smaller ions such as those of $(MnX)^+$.

A typical spectrum is as illustrated by that of $p\text{-}FC_6H_4COC_5H_4Mn(CO)_3$ (Spectrum 7-3). The proposed fragmentation pattern (Fig. 7-5) is tentative but some of the decomposition paths are supported by observed metastables. Wherever a fluoride is present in an ionic species it is correspondingly compared with its chloride analogue. The latter is readily identified because of the natural abundance of isotopes ^{35}Cl and ^{37}Cl (3:1). In this way, many of the halogen containing species are identified. The loss of C_5H_4CO appears to be the most significant decomposition path following the formation of $(P\text{-}3CO)^+$. The low abundance of the other ionic species suggests that the rings are comparatively stable. A surprisingly high abundance of Mn^+, however, has been observed (100%).

The spectra of ortho substituted complexes are more complex. Unlike the meta and para substituents, the ortho substituents are good leaving groups. Ions such as $(MnF)^+$ have been observed in relatively high abundance (19%) (Spectrum 7-4). Fig. 7-6 is a general fragmentation pattern observed for $o\text{-}FC_6H_4COC_5H_4Mn(CO)_3$. It is readily observed that the loss of X is in the form of HX. The loss of OH as a molecule of H_2O, for example, has been observed even before all the three CO molecules are removed; a



Spectrum 7-4



Spectrum 7-3

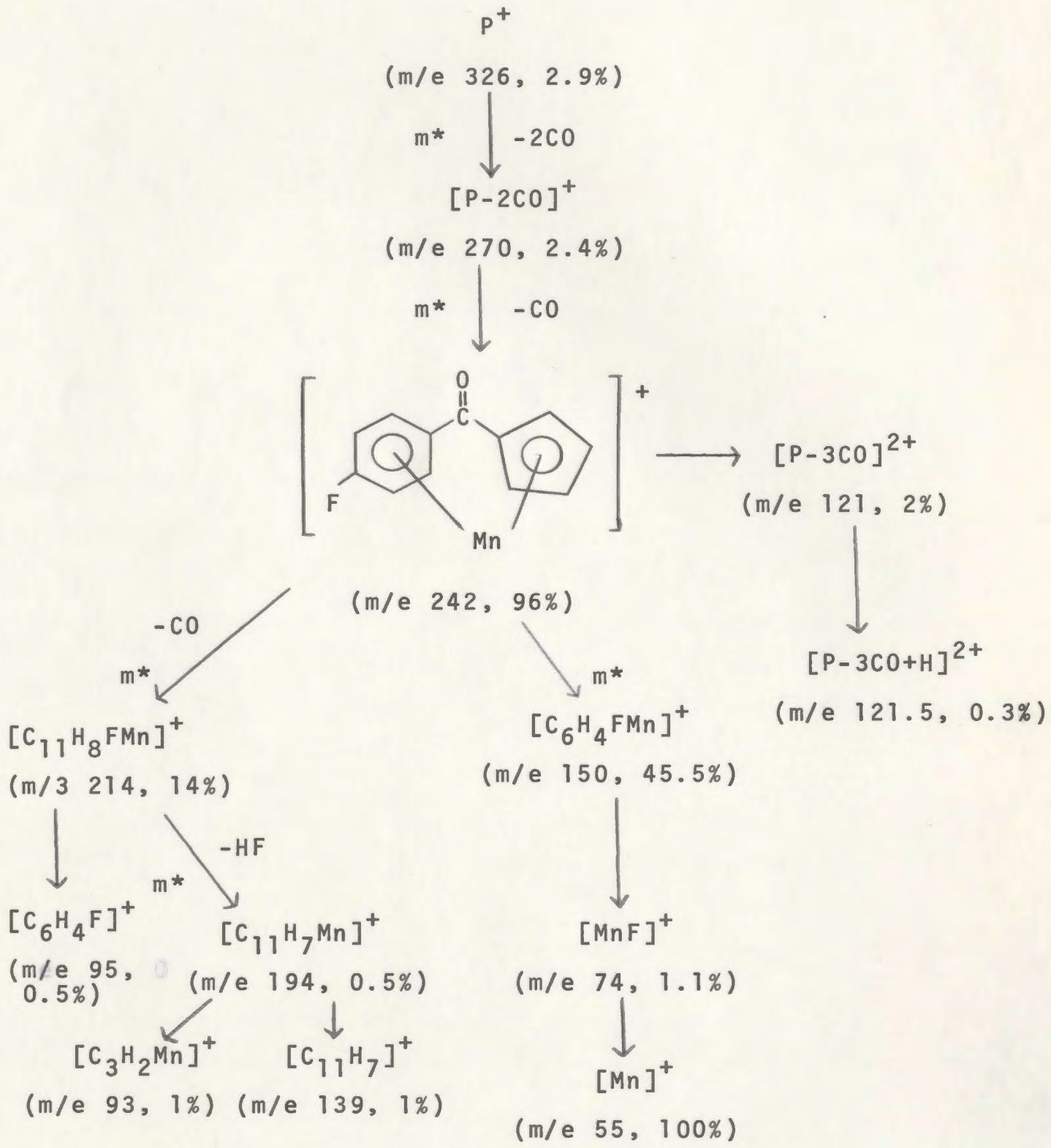


Fig. 7-5

Fragmentation Scheme of p-$FC_6H_4COC_5H_4Mn(CO)_3$

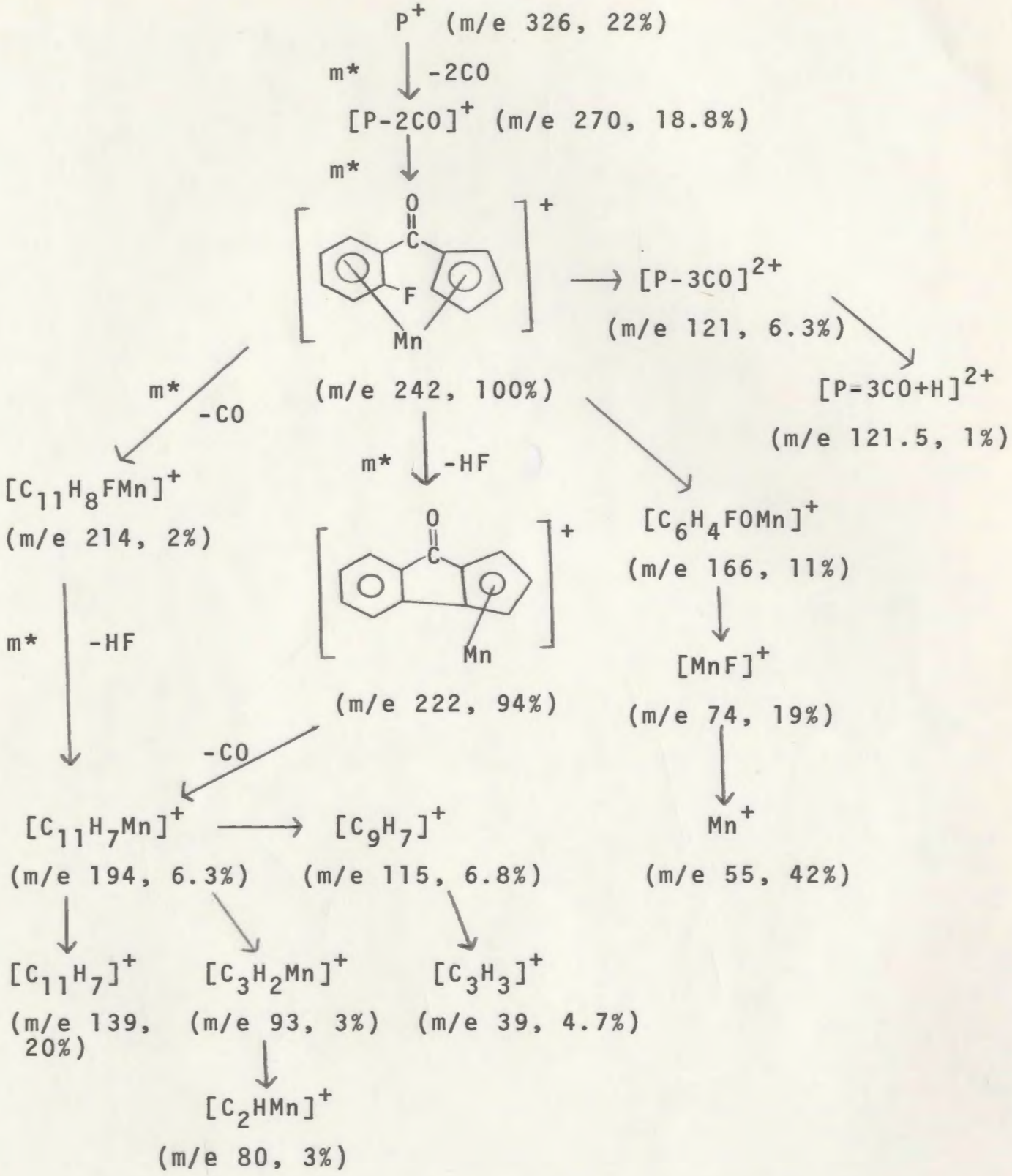
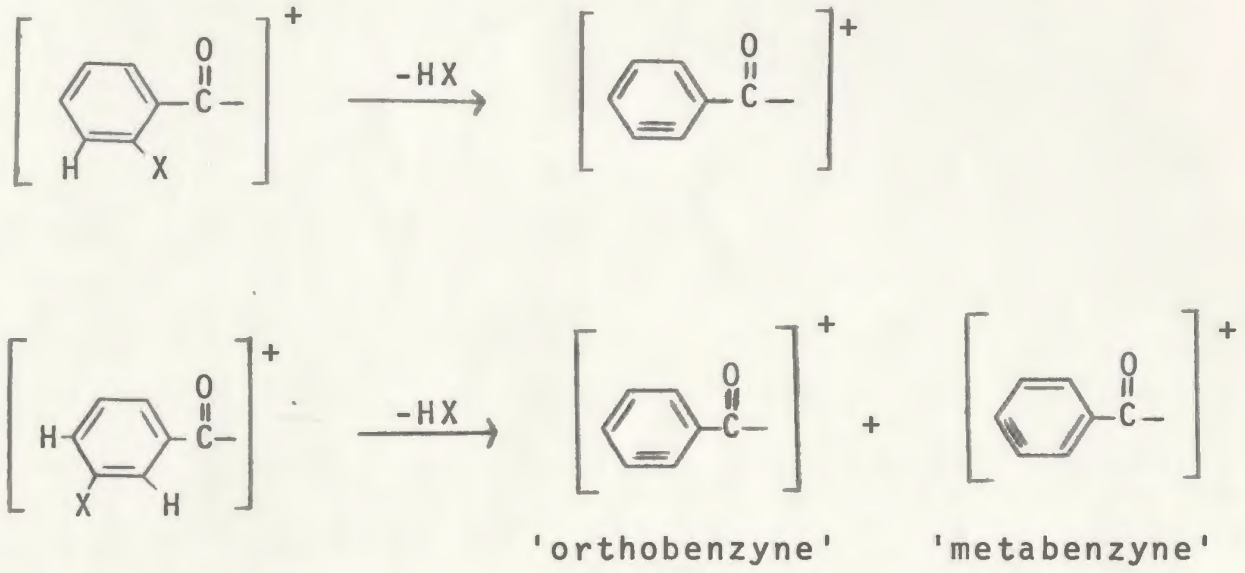


Fig. 7-6

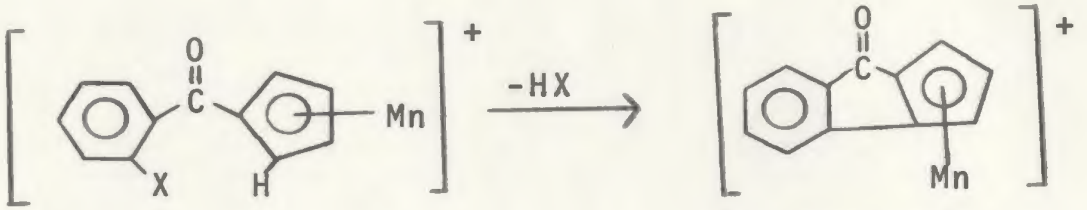
Fragmentation Scheme of o-$FC_6H_4COC_5H_4Mn(CO)_3$

phenomenon not observed in any of the other complexes studied. The relative ease of removal of HX in the ortho complex as compared to the meta and para analogues cannot be explained by the formation of a benzyne type of ion.



A random removal of a HX molecule from the meta substituted complex is expected to give a near statistical ratio of 1:1 of ortho to meta benzyne type of ion. The fact that the relative abundance of $(P-3CO-HF)^+$ observed in the ortho complex (94%) to the meta complex (5%) is about 18:1 suggests that this assumption is inadequate. Furthermore, there is no reason why such an intermediate has not been observed in the para analogue. Alternatively, these results can be explained by some form of ring closure mechanism in which the hydrogen atom of the removed HX molecule comes from the α-position of the cyclopentadienyl ring instead

of the arene ring.

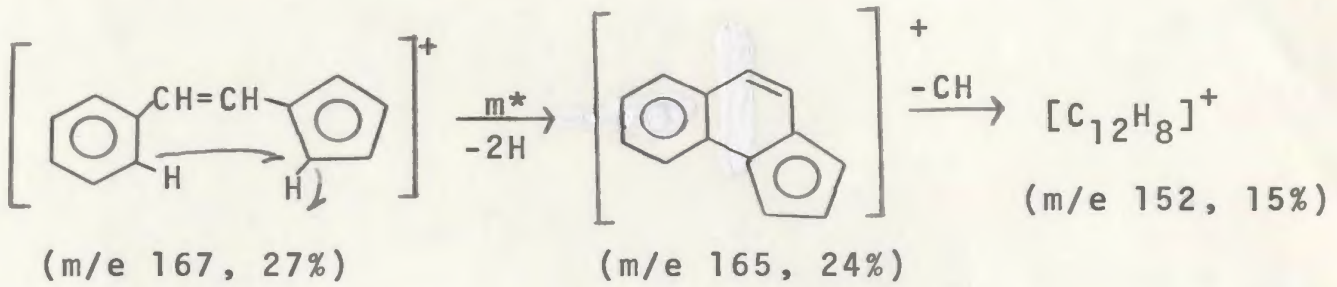


(m/e 222)

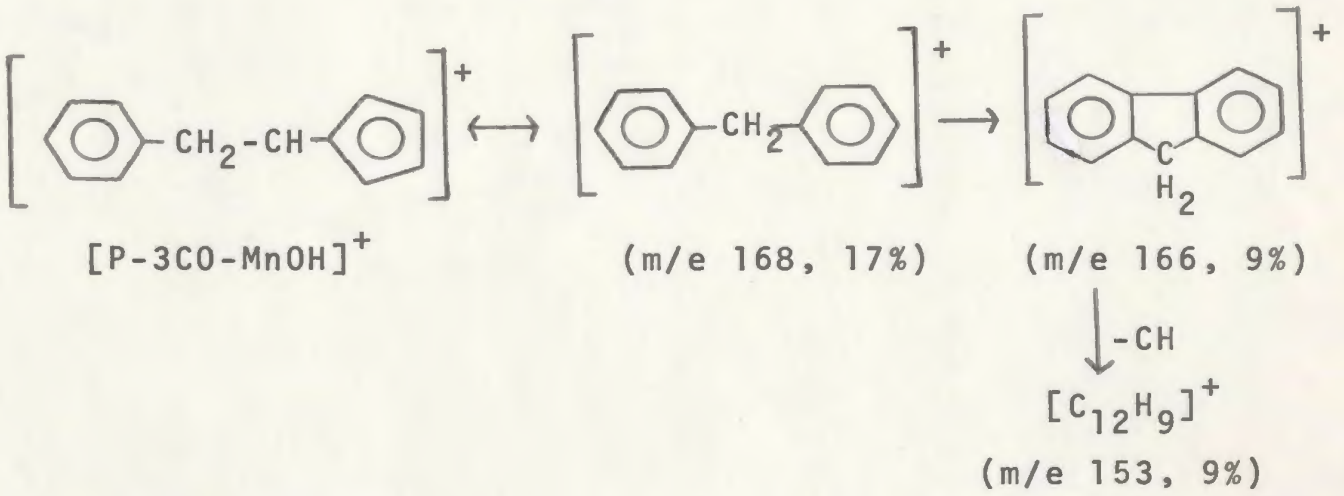
SOME MISCELLANEOUS SPECTRA

$C_6H_5CH_2CH(OH)C_5H_4Mn(CO)_3$

The mass spectrum of this complex shows low abundance of ions corresponding to $(P-H_2O)^+$ (0.5%) and $(P-2CO-H_2O)^+$ (0.8%) but no $(P-CO-H_2O)^+$ is observed. This further shows that the loss of the three CO molecules is not a stepwise process. The loss of a molecule of H_2O is important only after the loss of the three CO molecules. The ion $(P-3CO-H_2O)^+$ (m/e 222) is then the most abundant. The loss of the ketonic CO group is not observed at all and it is noteworthy that the next most important fragmentation is the loss of neutral metal. This implies that the ionisation potential of the ligand is probably lower than that of manganese atom. The loss of two hydrogen atoms from this ion $(P-3CO-H_2O-Mn)^+$ suggests that some form of ring closure mechanism has perhaps taken place.



The above mechanism accounts for the peaks at m/e 167, 165, and 152 but not 168 and 153. It is possible that an independent ring closure process following the loss of a MnOH group instead of H_2O molecule then a Mn atom, has taken place.



$C_6H_5CH=CHC_5H_4Mn(CO)_3$

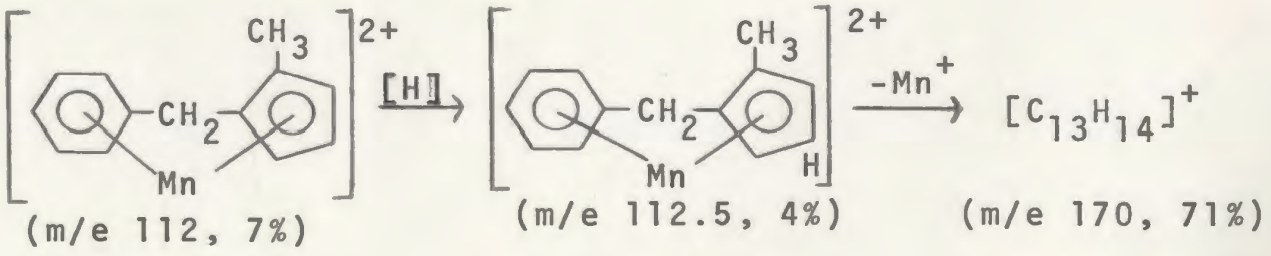
The fragmentation pattern of this complex is very similar to that of $C_6H_5CH_2CH(OH)C_5H_4Mn(CO)_3$ except for the initial loss of H_2O molecule which is not observed here. The base peak is at m/e 222 corresponding to the

ion $(P-3CO)^+$. Ring fusion follows after the loss of manganese in a way similar to that previously discussed.

$C_6H_5CH_2C_5H_3(X)Mn(CO)_3$

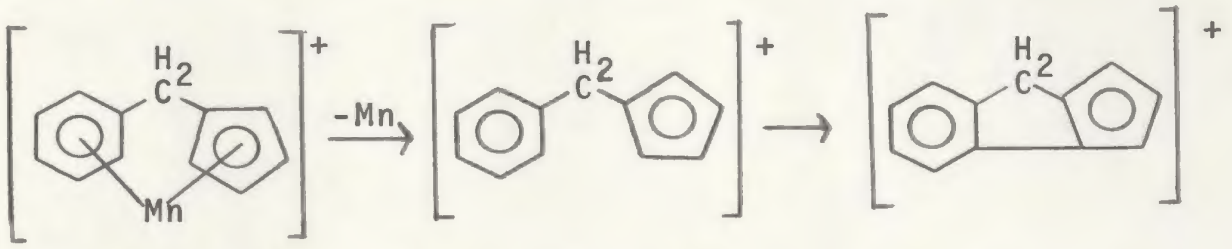
The spectra of complexes where X = H, (I); X = α-CH_3 (II); X = β-CH_3 (III), have been studied. The loss of CO molecules is a two-step process. Apparently the methyl substituent on the cyclopentadienyl ring seems to have quite an effect on the subsequent decomposition of the $(P-3CO)^+$ ion. Complex (II) appears to behave differently from the other two and the main features are summarised below:

(a) A very strong peak at m/e 170 has been observed for complex (II) (71%) whereas the abundance of this ion in complexes (I) and (III) is about 5%. This ion is attributed to $(P-3CO-Mn+H)^+$. It is difficult to account for the extra hydrogen without assuming some form of ion--molecule reaction. Perhaps a doubly charged ion is first formed which then reacts with a neutral species to give another doubly charged ion. Subsequent loss of manganese ion gives the observed ion.



(m/e 112, 7%) (m/e 112.5, 4%) (m/e 170, 71%)

(b) The relative abundance of $(C_7H_7)^+$ ion in complexes (I) (1.7%), (II) (100%), and (III) (13%) suggests that the cleavage of the cyclopentadienyl-C bond is most predominant in complex (II). Probably, the methyl substituent at the α-position promotes such a cleavage. The spectra of complexes (I) and (III) are consistent with a ring closure process as shown below.



(m/e 210, 100%) (m/e 155, 37%) (m/e 153, 10%)

No ions corresponding to $(C_7H_7Mn)^+$ are observed in all three structures, instead an ion attributable to $(C_6H_5Mn)^+$ (m/e 132) is observed for (I) (30%) and (III) (13%). The fact that this ion is observed in both the unsubstituted cyclopentadienyl derivative and the methyl substituted analogue suggests that the C_6H_5 group is most likely to have come from the phenyl ring. This implies that cleavage between the phenyl-C bond is more favourable than cyclopentadienyl-C bond.

FRAGMENTATION OF SOME Π-CHROMIUM TRICARBONYL COMPLEXES.

The loss of CO molecules appears to be a combination of a stepwise and a two-step process. Though metastables for the loss of consecutive CO molecules have been observed for all but one, the relative abundance of $(P-CO)^+$ (3-4%) is sufficient to suggest that the loss of one CO molecule has taken place. The loss of carbonyls from $Cr(CO)_3$ as a stepwise process is a better explanation than to assume that both the $Mn(CO)_3$ and $Cr(CO)_3$ groups undergo two step mechanisms. However, it is true that the loss of the three CO molecules from $Cr(CO)_3$ is definitely not a spontaneous one step process as observed in the systems studied by Cais[21].

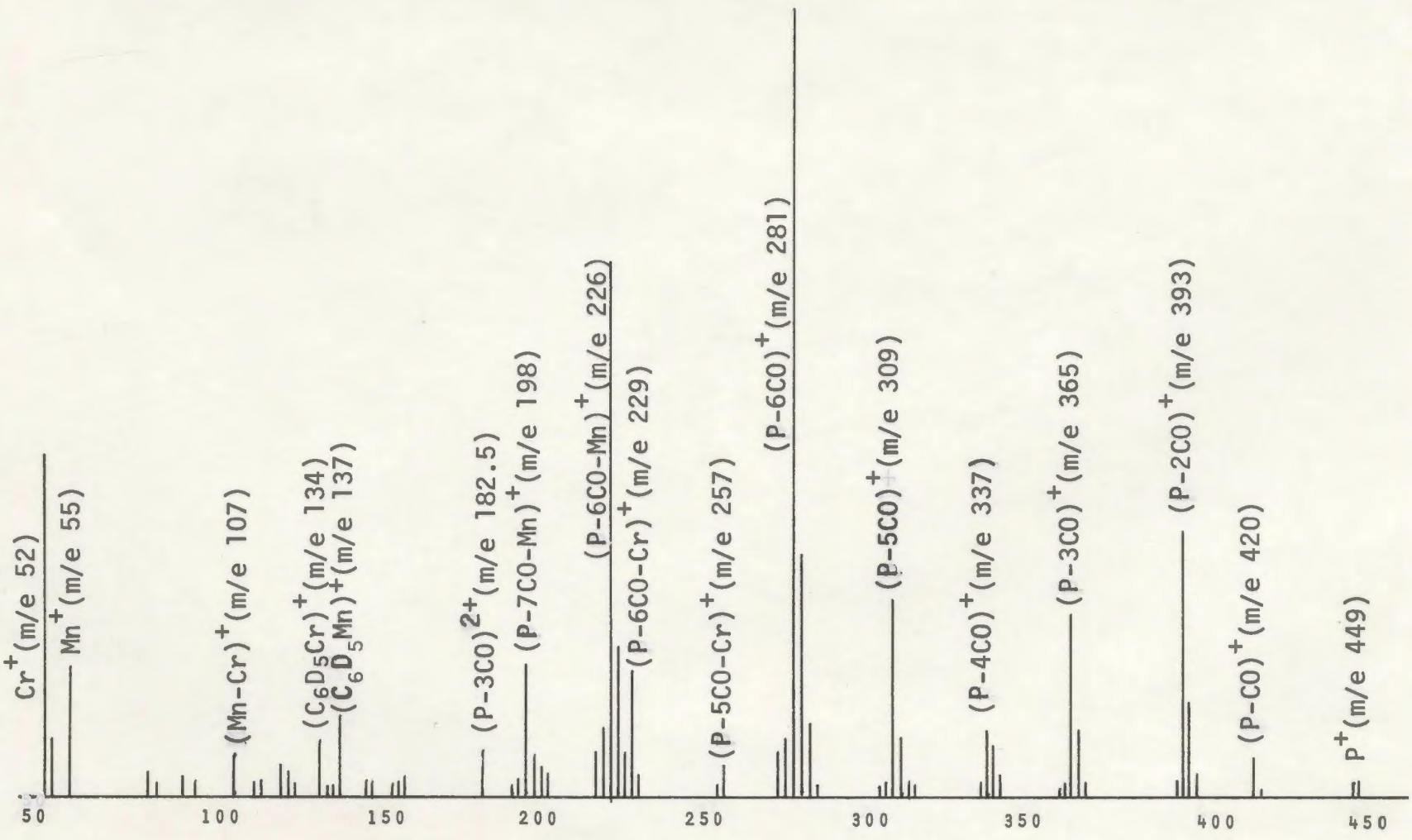
The relative abundance of $(P-nCO)^+$ in these complexes appears to follow a set trend of decreasing abundance, i.e.

$$(P-6CO)^+ > (P-2CO)^+ > (P-5CO)^+ \sim (P-3CO)^+ > (P-CO)^+ \sim P^+$$

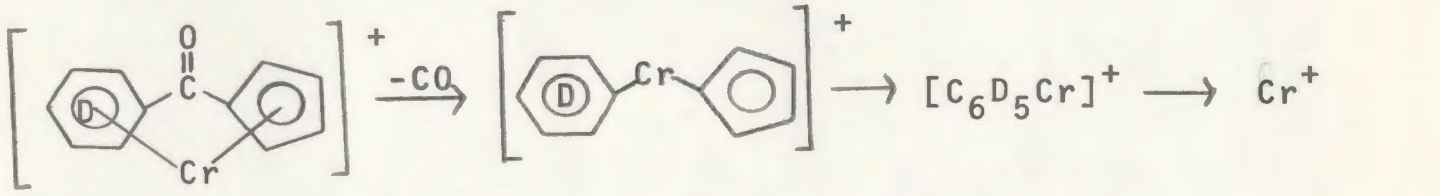
A typical spectrum of such complexes is shown in Spectrum 7-5. The relative abundance of $(P-6CO-Mn)^+$ is always greater than that of $(P-6CO-Cr)^+$ which suggests that the former is more stable than the latter. Perhaps the Cr--phenyl bond is stronger than the Mn-cyclopentadienyl bond. Notice also that only the ions $(C_6H_5Cr)^+$ and $(C_6H_5Mn)^+$

Spectrum 7-5

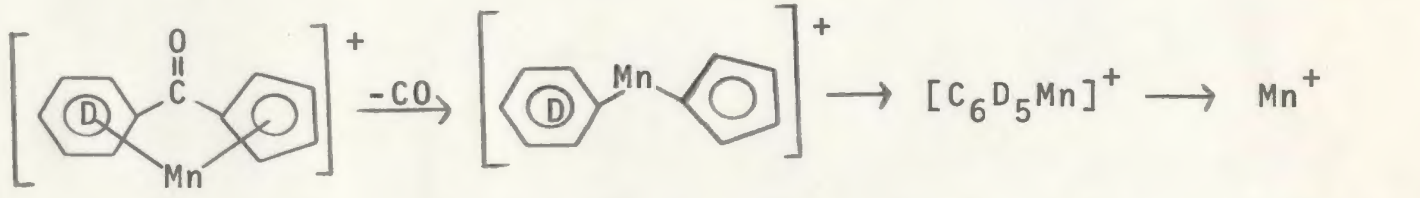
Normalised Spectrum of $[(CO)_3CrC_6H_5COC_5H_4Mn(CO)_3$



have been observed. No ions corresponding to $(C_5H_4Cr)^+$ or $(C_5H_4Mn)^+$ are detected. This implies that cleavage of the metal-cyclopentadienyl bond is easier than cleavage of metal-phenyl bond and is consistent with the fragmentation pattern shown below



(m/e 226, 69%) (m/e 198, 14%) (m/e 134, 6.4%) (m/e 52, 45.4%)



(m/e 229, 14.5%) (m/e 201, 1.1%) (m/e 137, 9.2%) (m/e 55, 15%)

This conclusion does not contradict the results obtained by Müller[16] and Denning[9] in which they found that the mass spectra of $C_6H_6MC_5H_5$ (M = Mn or Cr) seem to suggest that the ion $(C_6H_6M)^+$ is less stable than that of $(C_5H_5M)^+$. Perhaps these ions are more π in character than the ions

$(C_6H_5M)^+$ and $(C_5H_4M)^+$ which are probably more σ. Moreover, it has been observed that generally the $(C_5H_4Mn)^+$ ion shows very low abundance in all the cyclopentadienylmanganese tricarbonyl derivatives studied[14].

It is perhaps worthwhile to note that the spectra of these complexes containing two different metal-carbonyl moieties always show a peak at m/e 107 (ca. 5%). This is probably due to the formation of a bimetallic ionic species $(Cr\text{-}Mn)^+$. Similar type of bimetallic ions have also been observed by Cais et al.[20] in mixed metal-carbonyl complexes of the type $(Fe(CO)_3L(Cr(CO)_3)$ where L is some aromatic ligand.

CONCLUSION

The fragmentation of the complexes studied here shows that the decomposition of the ligand is only important after the loss of all the CO molecules from the $M(CO)_3$ moieties. This loss of CO molecules is found to be a two-step process for the $Mn(CO)_3$ moiety and stepwise for the $Cr(CO)_3$ moiety.

In complexes which do not have a $Cr(CO)_3$ group complexed to the arene ring, the ion, $(P\text{-}3CO)^+$, is found to be very stable and often most abundant. It is proposed

that this ion is probably stabilised by the participation of the manganese atom in the π-bonding of the arene ring. The fragmentation pattern of these complexes is also dependent on the substituent at the ligand. Whereas a methyl group on the phenyl ring tends to stabilise the $(P-3CO)^+$ ion, the halogen group tends to destabilise it. Most of the smaller hydrocarbon fragments have been identified to have originated from the cyclopentadienyl ring which suggests very strongly that the cyclopentadienyl ring decomposes more readily than the benzene ring.

In complexes which have a $Cr(CO)_3$ group complexed to the arene ring the $(P-6CO-Mn)^+$ ion is found to be four to five times more abundant than the $(P-6CO-Cr)^+$ ion. This implies that the Cr-phenyl bond is more readily cleaved than the Mn-cyclopentadienyl bond.

The mass spectra of non-conjugated systems show that the two aromatic rings in the ligand have a high tendency to fuse. In most cases, the positive charge remains on the fused ring and the metal is removed as a neutral species which is consistent with the fragmentation of bis(π-indenyl)iron observed by King[7].

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GENERAL CONCLUSION

Some derivatives of cyclopentadienylmanganese tricarbonyl have been synthesised. Spectroscopic study of these derivatives gives a better understanding of the nature of the π-metal-ligand bond involved. A qualitative M.O. treatment has been successfully applied to interpret the electronic transmission effects in these systems.

The infrared spectral studies show that substituent effects are transmitted from the aromatic ligand to the C-O bond of the $M(CO)_3$ group π-complexed to the ligand. This is evident from the observed changes in ν(CO) frequencies with change of substituents. Though this change is small, it is nevertheless significant. This indicates that there is a substantial amount of overlap between the π-orbitals of the ring-metal bond with those of the M-C-O bond. A more significant shift in the ketonic ν(CO) frequency is also observed which shows that the system is conjugated.

The decrease in the ketonic ν(CO) frequency observed when the arene ring is π-complexed with the $Cr(CO)_3$ group is interpreted as a withdrawal of π-electron by the $Cr(CO)_3$ group from the aromatic ligand. This conclusion is in agreement with ESR spectral results which show that the $Cr(CO)_3$ group is capable of withdrawing a large fraction of the spin density from the manganese atom of the

$-C_5H_4Mn(CO)_3$ moiety to itself. Since a corresponding decrease in the spin density on the arene ring is also observed, the spin density is believed to be more localised on the chromium atom. This is supported by EHMO calculations which shows that the spin density is mainly found on the ketonic carbonyl and the metal atoms of the $M(CO)_3$ groups. The high degree of delocalisation of the spin in the system shows that the lone electron resides mainly in the vacant π-orbitals of the system and not in the σ-orbitals.

The relatively higher spin density at the para and ortho protons than at the meta protons of the ring is consistent with the higher electron density at the latter protons which makes the occupation of the lone electron in these positions less favourable. The same conclusion is obtained from NMR spectral studies which show that the chemical shifts of the meta protons are observed at higher fields than those of the ortho and para protons. This difference in electron densities between these protons is more apparent in the π-$Cr(CO)_3$ complexes. This suggests that the $Cr(CO)_3$ group has a more stabilised configuration in which the three CO molecules lie immediately above the ortho and para positions of the mono-substituted benzene ring.

The withdrawal of π-electrons from the arene ring by the $Cr(CO)_3$ group is not very apparent from NMR studies. However, the upfield shift observed for the

arene proton resonances when the $Cr(CO)_3$ group is π-complexed to the ring suggests that the $Cr(CO)_3$ group is capable of localising a high electron density between the Cr-ring bond. In other words, this bond is stabilised by the increased overlap in the a_1 and e_1 bonding orbitals. Perhaps this effect contributes significantly to the shielding of the arene protons.

Generally, substituents at the ortho or α-positions of the phenyl or cyclopentadienyl ring tend to reduce the delocalisation of π-electrons in the conjugated system. This is attributed mainly to the steric effect of the substituent which reduces the coplanarity of the π-orbitals.

Suggested Further Work.

The present work deals with π-complexes of $Mn(CO)_3$ and $Cr(CO)_3$ moieties. This may be extended to include other moieties such as $Re(CO)_3$, $Mo(CO)_3$ and $W(CO)_3$. In addition, the aromatic ligands may also include heterocyclic ring systems like thiophene, pyrrole and furan. Such studies may lead to a better understanding of the nature of the π-bonding between the metal and the ligand. It will also be of interest to study the electronic effects of such systems in which the CO molecules are systematically replaced by ligands such as PPh_3 and C_2H_4.

The lack of accurate energy levels in molecular orbital models makes it difficult to assign unambiguously

ultraviolet absorption bands of these π-metal carbonyl complexes. Perhaps a careful and systematic study of the appearance potentials and ionisation potentials of these complexes by mass spectrometry will help to remedy this situation. Such data may give us a better approximation to the ordering of the energy levels in the molecular orbitals which to date is still lacking.